STUDIES ON INORGANIC AND ORGANIC ION EXCHANGERS

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Certificate

This is to certify that the work embodied in this thesis entitled "Studies on Inorganic and Organic Ion Exchangers", is original work carried out by Mr. Abdul Aziz Ansari under my supervision and is suitable for submission for the award of Ph.D. degree in Chemistry of this University.

(J.P. Rawat)

TO

without whose sacrifice I could
not have undertaken this work

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C O N T E N T S

LIST OF PUBLICATIONS

1. Synthesis and ion exchange properties of sodium stannosilicate: A silver selective inorganic ion exchanger.
   Bull. Chem. Soc. Jpn., (In press)

2. Redox ion exchanger fuel cell.
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   Solvent Extn. Ion Exch., (Comm.)

4. Sorption equilibria of lead(II) on some Indian soils: The natural ion exchangers.
   Colloids and Surfaces, (In press)

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Chapter I

Introduction

Ion exchange is one of the most versatile techniques of separation science. It is at present, an standard analytical tool and is widely used in inorganic, organic and biochemical separations. It offers many advantages over the classical methods of separation such as precipitation, distillation and filteration. This technique can be applied to both micro as well as macro analysis and may serve even for the routine analysis. It demands less skill and judgement from the analyst than many other methods. Furthermore, a shorter time is needed and the components can subsequently be determined by rapid instrumental or titrimetric methods. It is of great significance when one is concerned with the separation of ions of similar properties or the systems which are troublesome or impossible to analyze by other methods.

In laboratories ion exchangers are being used as an important tool to solve new problems that are placed by our industrialists and scientists. All over the world numerous ion exchanger plants are in operation for developing the separation of various mixtures of inorganic, organic and biological interest. Rapid and accurate determination of the constituents of a sample or contaminants of alloys of complicated compositions,

biological substances and fission products of radioactive elements has become possible by the use of ion exchangers. It has made possible the chromatographic separation of very complicated mixtures. This technique has been used to solve previously unsolvable problems such as the separation of rare earths and recovery of rare elements. The use of ion exchangers on large scale may provide mankind with pure water and may be useful for the concentration and extraction of important metals and raw materials which are becoming more and more difficult of produce. Ion exchange has established itself as one of the most powerful techniques in the field of water analysis, thus prooving its worth in water pollution control.

Soil, an inexpensive, natural and easily available material was for the first time recognised as an ion exchange material. Nearly 150 years ago an English landowner H.S. Thompson was interested to study the loss of ammonia from manure heaps. He engaged a York scientist named Spence to investigate this loss. Spence discovered this loss as an exchange process between calcium (from soil) and ammonia (from manure).

$$Ca^{2+}(soil) + (NH_4)_2\ SO_4 \rightleftharpoons NH_4^+\ (soil) + CaSO_4 \quad ....(1)$$

Spence reported his discoveries to the Royal Agricultural Society[1]. These were further confirmed by another agricultural chemist G.T. Way[2], who described this exchange by the name of "base exchange". The base exchange in soils was found to be reversible and stoichiometric. This phenomena could not be elaborated further as much was not known about the ionic nature of solutions and the crystal structure and composition of the clay minerals present in the soil. Many hypotheses were given to explain this exchange in soils[3], but ultimately it was traced mainly due to presence of aluminosilicates[4,5]. According to Lamberg[6] and Weigner[7] the materials responsible for the exchange in soils were mainly clays, zeolites, glauconites, humins and humic acid. The glauconites are also aluminosilicates analogous to the zeolites which possess exchangeable potassium and considerable capacity. The first aluminosilicates were synthesized by Harms and Rumpler[8] in 1903. The two principal causes responsible for ion exchange property of soils are organic matter and clay minerals. The soils rich in organic matter contain humins and humic acid which on decomposition produce a wide variety of organic species possessing -OH or -COOH groups. These groups are responsible for the ion exchange property in such soils. The soils which do not contain

much organic matter or whose organic matter has been destroyed by the treatment of hydrogenperoxide also possess a considerable ion exchange property due to the presence of crystallographic surfaces (clay minerals) with exchangeable sites.

Ion exchange is considered as a reversible process in which cations or anions are exchanged stoichiometrically between the ion exchanger and solution phases, when they are placed in close contact with each other. When an ion exchanger in counter ion A form is placed in a solution of another counter ion B then the ion exchange process may be written as

$$\bar{A} + B \rightleftharpoons \bar{B} + A \qquad \ldots\ (2)$$

where the barred quantities refer to the exchanger phase and unbarred to the solution phase.

Cation exchange in soils are of great importance as it can alter the availability of several micronutrients[9]. In soils a number of cations may be present in trace quantities, both beneficial as well as hazardous. An study of cation exchange in soils may give an idea about the capability of the soils to store[10] and supply[11] the nutrient elements to plants. These studies are useful in relation to plant growth because the metal ions may

increase the supply of some nutrients in plants while decrease others[9]. Soil pollution has always commanded a great interest. The land disposal of industrial and municipal sludges are of great concern as the content of heavy metals such as lead, cadmium, mercury and several others in sludges can be high.[12] Hence there is a potential hazard of contaminating soils with excess amount of these metals, which have been retained in soils by ion exchange. The exchange behaviour of heavy metals in soils has been investigated by Lagerwerff and Brower.[13] Amphlett and McDonald[14] studied the ion exchange equilibria of clay mineral fraction of a soil from English Lower greensand series. These soils were found to exhibit a well defined affinity series and their overall properties were expected to depend on the clay mineral fraction of the soils.

The clay minerals are aluminosilcates, having alternating, parallel, two dimensional layers formed from silicate tetrahedra and aluminate octahedra.[15] The chemical as well as physical properties of clays depend upon the disposition of these layers and the extent and nature of isomorphous substitution within the layers. The cation exchange capacity in clays is partly due to exchange at the edges and corners of the layers and to a greater extent due to replacement of cations in the interlayer spaces.

However, exchange in clay minerals is non-stoichiometric. The clays having similar structures but different degrees of isomorphous substitution possess an appreciable variation in the ion exchange capacity. They are unstable at higher temperatures due to irreversible loss of water ie. structural water is lost and their ion exchange capacity decreases. They swell appreciably in water when the concentration of interlayer cations is high. The clays possess a well defined affinity series[16] and in general the affinity for cations increases in the order of decreasing hydrated ionic radius. Their stability towards acid solutions is also limited due to breakdown of the aluminosilicate structure in acids. Hydrogen form of the clays may be prepared by slurring them with a cation exchange resin in hydrogen form. Clay minerals can be used as an ion exchange media, particularly when one is concerned with specificity, cheapness or stability towards radiation or high temperature water. After some preliminary treatment montmorillonite may be used for the treatment of radioactive waste solutions. Vermiculite needs no preparation for this purpose.

The discovery of exchange in soils due to presence of aluminosilicates led to the use of natural materials for softening of water. Gans tried to recover gold from

sea water but could not succeed because of nonavailability of a suitable ion exchange material for this purpose. The practical utility of ion exchange phenomena was recognised by Gans and his coworkers[17] for water softening. They developed synthetic zeolites or permutits for this purpose, which are synthetic aluminosilicates with exchangeable sodium. When hard water is passed through this material, sodium is replaced by calcium and then softened water contains innocuous sodium salt. The exchanger may be regenerated after use, by passing a concentrated solution of sodium salt.

Synthetic zeolites are prepared in several ways. For example by fusing together mixtures of soda, potash, felspar and kaoline (fusion permutits) or by a controlled addition of alkali to acid solutions of aluminium sulfate and sodium silicate (gel permutits). Fusion permutits resemble natural zeolites whereas gel permutits appear like silica gel. Synthetic crystalline zeolites are prepared by slow hydrothermal crystallization at elevated temperatures from solutions of silica, alumina and alkali. Various zeolites with completely regular structure have been prepared by several workers.[18-25]

Several analogues of the zeolites have been prepared by similar methods. Barrer[25] has prepared aluminogermanate

by replacing silicon with germanium. Sodium gallosilicate has been prepared by Selbin and Mason.[27] Gallocarbonates have been prepared by reacting together solutions of sodium gallate and sodium bicarbonate.[28] Ammonium tungstosilicate[29] has been prepared for chromatographic separation of UO_2^+ from Cs^+, Eu^{3+}, La^{3+} and Bi^{3+}. This method was designed for fission product and uranium ore analysis. Ferrosilicate[30] and other sodium metallosilicates[31] have also been synthesized. Fusion permutits have been prepared in which silicon was partially or completely replaced by other tetravalent elements such as titanium and tin and aluminium by other trivalent elements such as iron, mangnese, vanadium and phosphorus.[32,33] However, the properties of these products were unsatisfactory. Silicates of a number of elements such as zirconium[34], titanium[35], bismuth[36], ferric[37], zinc[38], tin[39] and antimony[40] have been synthesized and studied for their ion exchange properties.

The zeolites are crystalline aluminosilicates with ion exchange properties. They are characteristic representatives of most of the natural ion exchange minerals. The structure of zeolites are build up of AlO_4^{5-} and SiO_4^{4-} tetrahedra which have their oxygen atoms in common. These tetrahedral groupings share their corners, edges and

faces to give a condensed structure. Zeolites may exist as fibrous, lamellar or rigid three dimensional structures. The zeolites with three dimensional structures have been extensively studied by Barrer.[41] Their frameworks are open with channels and interconnecting cavities in the aluminosilicate lattice. The negative charge due to AlO_4^{5-} grouping is balanced by alkali or alkaline earth metal ions which are present as counter ions in the channels of the lattice framework. These counter ions can be replaced by other cations. The narrow, rigid and strictly uniform pore structure of the zeolites gives them a pronounced "sieve action" on a molecular scale. Large cations such as quaternary ammonium ions[42] and large nonelectrolyte molecules[43,44,46] which are larger than the openings in crystal framework are completely excluded whereas small molecules are sorbed or exchanged. Even inorganic cations such as Cs^+ are partially or completely excluded by several zeolites.[18,43,48] Pore size of the zeolites can be adjusted to a certain degree by replacing the counter ions by other ions. A wide range of chromatographic separations can be achieved by choosing a suitable zeolite and its cationic forms. For example Cs^+ has been separated from other alkali metals on analcite[45]. Molecular sieve properties are now being used on industrial scale, since the development of Linde

molecular sieves. Linde molecular sieves were synthesized and studied by Barrer[26] and Breck.[46] Saha[47] have studied the use of natural and synthetic zeolites for fractionation, sorption and catalysis.

Selectivity in the zeolites have been studied by Barrer.[48] In the absence of ionic sieve action in zeolites, selectivity towards certain ions may still exist due to differing thermodynamic affinities. The zeolite selectivity have been utilized in a number of instances. Silver can be recovered under suitable conditions using basic sodalite. Mineral clinoptilolite may be used for the removal of trace concentrations of caesium from solutions containing a high concentration of sodium. It has been used as an adsorbent for the treatment of low activity radioactive waste solutions.[49] Synthetic ultramarines have been used to separate ^{223}Fr from its actinium parent and other activities.[50]

The stability of zeolites in acid solutions is limited. The anionic framework of the zeolites is chemically unstable and breaks down in acid solutions with the precipitation of hydrated silica, leaving aluminium in solution. This causes a difficulty in the preparation of H^+ form of the zeolites. However, ion exchange phenomena may be utilized for this purpose.

For example H^+ form analcite is prepared by treating silver analcite with an aqueous solution of halide of a metal ion which is too large to enter the structure of analcite.[45] A precipitate of silver halide is formed in the solution. The metal ion and hydroxide ion remain in the solution and analcite in H^+ form is obtained.

A serch for stable ion exchanger was started to overcome the limitations possessed by zeolites and clays. In 1931 Kullgren found that copper was taken up by sulfite cellulose when the cellulose was washed with distilled water.[51] He used this material for the removal of copper present in water as a contaminant. Organic ion exchangers were recognised after an interesting discovery of Adams and Holmes in 1935. They found that crushed phonograph records exhibit ion exchange properties. This led them to the synthesis of organic ion exchange resins[52] which exhibited an improved properties over the previously known ion exchangers. These resins consist of three dimensional networks of polymeric chains cross-linked with short chains containing ionizable functional groups. Various improvements were made in these resins. A typical resin is prepared by a polymerization of styrene and divinyl-benzene. The number of cross-linkage is governed by divenylbenzene to styrene ratio. A representative type

of strong cation exchange resin is Dowex 50 W X 8, manufactured by Dow Chemical Co., Midland, Mich. Organic ion exchange resins are stable towards acids and elegant to handle. Their structure can be varied as desired. An increase in cross-linkage increases the rigidity, reduces swelling and reduces the solubility of polymeric structure. Organic resins have been used in laboratories and industries for separations, recoveries of metals, purification of water, concentration of electrolytes and elucidation of the mechanism of great many reactions. Several commercial resins, both cation (strong and weak acid) and anion (strong and weak base) exchangers are available for these purposes. A third type is amphoteric ion exchange resin with only a few applications.

Organic ion exchangers also suffer from certain limitations. They are unstable in aqueous system at high temperatures and in the presence of ionizing radiations. This led to a revived interest in inorganic ion exchangers. Inorganic ion exchangers are unaffected by ionizing radiations and considerably temperature resistant. This makes them suitable for use in reactor technology. Their rigid structure makes them more suitable for separation of ions on the basis of different pore sizes. They can also be used as ionic or molecular sieves. High selectivity and temperature resistance offer them an advantage for use

as ion exchange membranes. Their selectivity has also been utilized for the preparation of ion selective electrodes which has now become an important tool for solving various analytical problems.

Systematic and fundamental studies on inorganic ion exchangers commenced in 1943 with the application of zirconium phosphate to the separation of uranium and plutonium from fission products.[53] Zirconium phosphate is perhaps the most studied inorganic ion exchanger. Other inorganic ion exchangers with satisfactory properties have been prepared by combining group IV oxides with more acidic oxides of group V and VI. Various inorganic ion exchangers reported upto 1964 have been excellantly reviewed in a monograph of Amphlett[54] entitled "Inorganic Ion Exchangers" which has become a classic in this field. The different types of ion exchange materials are summarized in the following broad groups:

1. Clay minerals
2. Zeolites
3. Heteropoly acid salts, and
4. Hydrous oxides and Insoluble salts

Literature data on a new series of synthetic inorganic ion exchangers has been compiled by Ionescu[55] considering in this study the salts of heteropoly acids,

the oxides and hydroxides of polyvalent metals and some particular compounds such as polyphosphates, ferrocyano-molybdates and mixed ferrocyanides of light and heavy metals. Representative types of inorganic ion exchangers have been reviewed by Ito and Abe.[56] The theoretical aspects of ion exchange in the inorganic ion exchangers have been described by Marinsky.[57] The work done in the period between 1963 and 1970 have been summarized by Pekarek and Vesely[58,59] under the following categories:

1. Hydrous oxides
2. Acidic salts of polyvalent metals
3. Salts of heteropolyacids
4. Insoluble ferrocyanides
5. Synthetic aluminosilicates, and
6. Certain other substances

A review on zirconium phosphate ion exchangers, polybasic salts other than zirconium phosphate and the salts of heteropolyacids and hydrous oxides has been given by clearfield[60]. M. Abe[61] has summarized the ion exchange characteristics of salts containing polyvalent elements of group III, IV, V and VI. Marinsky[62] and Walton[63] have edited the reviews on the application of inorganic ion exchangers. Synthesis and application of inorganic ion exchangers have been reviewed by Walton[64-68]. The recent

trends in the field of ion exchange have been summarized in the "Journal of Chromatography", volume 102 (1974), which contains the papers presented at the third symposium on ion exchange held at Balatonfired (Hungary) May 28-31, 1974. The papers presented were divided into four sections:

1. Ion exchange materials
2. Theory of ion exchange
3. Analytical applications, and
4. Ion exchange technology

The synthesis of new materials have been reported by numerous authors defining different types of amorphous, poorly crystalline and crystalline materials. The zirconium phosphate is the most studied of all the ion exchangers. A review with the emphasis on zirconium phosphate has been recently presented by Gracia et al.[69] Recent work on inorganic ion exchange materials has been covered in a monograph of clearfield.[70] Recently, a comprehensive review on different types of synthetic inorganic ion exchangers and their properties have been reported.[71,72]

In addition to the materials mentioned so far, a number of other types of exchangers have been developed e.g. electron exchangers and redox ion exchangers. Electron

exchangers are solid oxidizing and reducing agents. They are, as a rule, resins with a cross-linked hydrocarbon matrix. They contain the species such as quinone/hydroquinone, forming a redox couple which can be reversibly oxidized or reduced. They can be regenerated by a suitable reducing (or oxidizing) agent after having been oxidized (or reduced) by a substrate.

Redox ion exchangers are conventional ion exchange resins containing reversible oxidation-reduction couples such as Fe^{3+}/Fe^{2+}, Cu^{2+}/Cu and methylene blue etc.[73-75] These redox couples are held by the ion exchange resins (e.g. Dowex 50, cation exchange resin) either as a counter ion or by sorption or complex formation. Duolite 5-10 is a commercial redox ion exchanger.

The behaviour of redox ion exchangers and electron exchangers is similar to that of the soluble oxidation-reduction couples. The redox potential of a couple is little affected by incorporation of the couple into a resin.[76,77] They possess some advantages over dissolved oxidizing or reducing agents. The most important advantage is their insolubility and hence they can be easily separated from the solution containing a substrate being oxidized or reduced. No contamination of the solution by these exchangers occur as only electrons and protons

are transferred between the exchanger and solution phases. The only possible change in solution, except for the redox reaction of the substrate, is a change in pH. Another advantage is that they can be readily regenerated after use by a suitable reducing or oxidizing agent.

Redox ion exchangers and electron exchangers are characterized by their redox capacity, redox potential and rate of the reaction. The redox capacity is the amount of a substrate being oxidized or reduced by a specified amount of the exchanger and is expressed in terms of the milliequivalents per gram of dry resin. The reaction rate determines the time required for the redox process under a given set of conditions. The standard redox potential indicates, which substrate can be reduced or oxidized. The redox potential of a couple in solution is defined as the electric potential difference between the solution of the redox couple and the standard hydrogen electrode. When two redox couples are in contact with one another, electrons can be transferred directly from one species to the other. In contrast, oxidation or reduction of a couple (transfer of electron) in a cell can only occur when the electrodes are short circuited so that electrons can flow from one half cell to the other. This flow of electron is an electric current which can do work. An equilibrium is attained when the two

couples have reached the same redox potential. The tendency of a redox couple say Fe^{3+}/Fe^{2+} to undergo oxidation or reduction depends on the concentration ratio of the oxidized and the reduced species (Fe^{3+} and Fe^{2+}). The redox potential thus is a function of this ratio. The standard redox potential of a redox couple is defined as the redox potential attained when the activity ratio of the oxidized and reduced species is unity.

Direct measurement of the redox potential of redox ion exchanger is not possible. For this purpose redox potential of a dissolved couple which is in equilibrium with the exchanger is measured and this potential is taken as the redox potential of the redox ion exchanger. Similarly standard redox potential of a redox ion exchanger is the redox potential of a dissolved redox couple which is in equilibrium with the exchanger when half of the species are oxidized and other half reduced. In its reduced form the redox ion exchanger can reduce the couples having a higher standard redox potential, whereas in its oxidized form it can oxidize the couples having a lower standard redox potential. A reducing agent with lower standard redox potential is used for reductive regeneration and an oxidizing agent with higher standard redox potential is used for oxidative regeneration. Standard redox potentials of some of the most common redox couples

are given by Latimer.[78] Some important redox ion exchangers are listed in Table I.1.

TABLE - I.1

Some important redox ion exchangers and their redox capacity

Serial No.	Name of Redox ion exchanger	Redox capacity meq g^{-1}	References
1.	Polymers of chlorophyll and haemin	-	79,80
2.	Polystyrene based redox resin	-	81
3.	Phosphonic acid type redox resin	-	81
4.	Tetrachlorohydroquinone	-	82
5.	p- benzoquinone melomine copolymer	4.00	83
6.	Zeolitic aluminosilicate	-	84
7.	Zirconium phospho Iodate	-	85
8.	Hydrazine sulfate sorbed zinc silicate	-	86
9.	Tetrachloroquinone	-	87
10.	Phosphomolybdovanadic acid	0.318	88
11.	Zirconium molybdovanadate	0.520	89
12.	Alkali and nickle ferrocyanide	-	90
13.	Phosphotungstovanadic acid	-	91
14.	Active carbon	-	92
15.	Zirconium peroxide metatungstate	-	93

The kinetics of redox ion exchange or electron exchange reactions have not been thoroughly investigated. Rate controlling step may be assumed either intraparticle diffusion or chemical reaction. The reaction rates are usually considerably lower than those of ion exchange. The half time of the reaction is often of the order of hours or days. Not all reactions which are possible according to standard redox potential proceed fast enough for practical applications. If diffusion is rate determining step then rate may be increased by reducing particle size and if it is chemical reaction then an increase in temperature may increase the rate.

For a complete description of a material as an ion exchanger its physical characterization should be made on the basis of the following properties:

1. Ion exchange capacity
2. Resistance towards acids and bases
3. Chemical composition, and
4. Potentiometric studies

Ion exchange capacity is one of the most fundamental properties for the characterization of an ion exchange material. The accepted way of characterizing the ion exchange capacity is by giving the number of ionogenic groups per specified amount of the ion

exchanger in H^+ or Cl^- form. The characteristic constant thus obtained is called scientific weight capacity and is expressed in terms of the milliequivalents per gram dry H^+ or Cl^- form exchanger. This is a characteristic constant of the ion exchange material and is independent of the experimental conditions. Other definitions are also used for various types of capacities, which depend on experimental conditions. The capacities of strong cation exchangers are readily determined by direct methods. The equilibrium ion exchange capacity of a strong cation exchanger is determined by direct titration of the exchanger in H^+ form with a strong base. This method is not reliable for the determination of ion exchange capacity of weak ion exchangers. In such cases the exchanger is first converted to H^+ form, then the equilibrium ion exchange capacity is determined by pH titrations. The maximum ion exchange capacity equal to the number of ionogenic groups per specified amount of the ion exchanger may be determined by simple column operation. In this method the electrolyte solution is passed over the ion exchanger in H^+ form at a slow rate and the liberated acid is titrated with a standard base solution. Other methods may also be used for the determination of ion exchange capacity of the solid ion exchanger. For example a gravimetric method,[94] which

offers for many ion exchangers the advantage of relatively high accuracy with a very simple equipment. This method is based only on the difference in weighing without any chemical determination of ions.

The ion exchange material must be studied for its resistance towards acids and bases to check its limitations.

The ion exchange materials may behave either as monofunctional or polyfunctional. The behaviour (monofunctional or polyfunctional) of ion exchangers can be determined by potentiometric titrations. The shape of the titration curve indicates whether the exchanger is monofunctional or polyfunctional. Such curves on zirconium phosphate with alkaline earth metal hydroxides have been studied by Alberti et al.[95] in detail. They observed that the titration curves are strongly affected by hydrolysis of the exchanger and precipitation of insoluble phosphates. The degree of conversion at which phosphate precipitation begins depends on the alkaline earth metal ions and the following values were obtained: Ca^{2+} 70% exchange, Sr^{2+} 80% exchange and Ba^{2+} 100% exchange. No exchange was found with $Mg(OH)_2$ due to its large hydrated ionic radius. Alberti et al.[96] also studied the forward and reverse Na^+ - K^+ exchange

isotherms and found that Na^+ - K^+ exchange in aqueous solution is a two step process with partial phase solubility. They also observed that zirconium phosphate prepared either by the refluxing procedure or by direct precipitation procedure, exhibit similar X-ray powder patterns but possess different ion exchange behaviour.[97]

The utility of the ion exchange materials can be developed on the basis of the following studies -

1. Distribution of counter ions between the exchanger and solution phases
2. Thermodynamics
3. Kinetics, and
4. Analytical applications

The affinity of an ion exchanger for a counter ion A is given quantitatively by the distribution coefficient, K_d which is defined as-

$$K_d = \frac{\text{No. of m.eq. of A in exchanger phase } g^{-1}}{\text{No. of m.eq. of A in solution phase } ml^{-1}} \quad \ldots\ldots(3)$$

The distribution of an ion between the exchanger and solution phases is a direct measure of selectivity. Usually, the ion exchanger takes up certain ions in

preference to the other counter ions present in the solution. The selectivity is an important factor for the study of separations and it may depend mainly on-

1. Donnan potential
2. Sieve action, and
3. Complex formation

The distribution coefficient is a practical guide to the separation procedure. By determining K_d values under varying experimental conditions, it is possible to select most suitable conditions for separating small amounts of various ions. The general use of distribution coefficient is made in the elution technique used in separations. The rate at which ions move in an ion exchange column depends on their distribution coefficient values. The ratio of the distribution coefficients of two different ions at low concentrations is called the separation factor which can be used to evaluate the ease of separating the two ions.

Thermodynamics is an appropriate means of describing the theoretical behaviour of ion exchange equilibria. Equilibria between the ion exchangers and solutions can be described in general by means of rigorous thermodynamics. This requires no model and no assumptions

about the mechanism of the ion exchange phenomena. However, rigorous thermodynamic treatment gives a minimum of information about the physical causes of the phenomena; therefore its practical utility is restricted. An interpretation in terms of the underlying physical forces requires a model. The properties of any particular model are reflected in form of the equations obtained and usually also in the physical interpretation in which these equations lead. This suggests that there are a number of different theoretical approaches. Two most approapriate theoretical approaches are usually applied for this purpose.

In the first approach more and more elaborate models are designed for deriving equations which reflect the action of various physical forces. These models have particular properties resembling those of ion exchangers. This approach gives a semiquantitative picture to understand the physical causes of the phenomena. However, the choice of the model is crucial and every commitment to a model with particular properties means a deviation from rigorous thermodynamics.

In the second approach various attempts have been made to correlate the activities, with some measurable quantities, with the thermodynamic equations.

The earliest approaches were based on semiemperical or emperical equations to fit the experimental results. Probably the first quantitative formulation of ion exchange equilibria was made by Gans.[98] For this purpose he used the law of mass action in its simplest form, without involving the concept of activity coefficient. This concept was accounted by Kielland.[99] He expressed the activity coefficient of the ions in exchanger phase in terms of a constant and the mole fractions of the ions in exchanger phase. Gaines and Thomas[100] gave a general treatment using an expression for the calculation of thermodynamic equilibrium constant which is a suitable choice for this purpose.

The thermodynamics of ion exchange on inorganic ion exchangers is considerably simple as compared with the organic ion exchange resins. This is because inorganic ion exchangers, particularly zeolites, possess a rigid structure, little swelling and relatively small changes in water content between different cationic forms of the exchanger. When an ion exchanger in counter ion A form is placed in a solution of counter ion B, an equilibrium is set up for the distribution of A and B between the exchanger and solution phases. The ion exchange process at equilibrium may be written as-

$$\bar{A} + B \rightleftharpoons \bar{B} + A \qquad \ldots.(4)$$

where the barred quantities refer to the exchanger phase and unbarred to the solution phase.

Ion exchange being a stoichiometric process will liberate an amount of counter ion A equivalent to the counter ion B taken up by the ion exchanger. For the sake of convenience, the effect of co-ions on the ion exchange equilibria may be neglected. The thermodynamic equilibrium constant for the ion exchange reaction is given by

$$K = \frac{\bar{a}_B \, a_A}{\bar{a}_A \, a_B} = \frac{[B][A]}{[A][B]} \cdot \frac{\gamma_B \, f_A}{\gamma_A \, f_B} \qquad \ldots.(5)$$

where γ represents the activity coefficient of ions in the exchanger phase and f the activity coefficient of ions in solution phase.

The thermodynamic equilibrium constant gives an information about the preferential uptake of counter ions by the ion exchanger.

The free energy change of the ion exchange reaction is obtained from the thermodynamic equilibrium constant using the equation-

$$\Delta G = - RT \ln K \qquad \ldots.(6)$$

where R is a universal gas constant and T the absolute temperature.

The selectivity of ions is governed by the lowering of free energy of the system. The enthalpy change of the system is evaluated by using Van't Hoff isochore. The change in enthalpy predicts whether the reaction is endothermic or exothermic. Enthalpy change of the system is directly related to changes in the number and strength of the bonds in the ion exchange process. The randomness of the ion exchange process may be predicted from the values of the free energy change and enthalpy change. The entropy change is calculated from the values of enthalpy change and free energy change at a given temperature. The overall entropy of the system reflects the extent of order produced during the ion exchange process. Hypothetical thermodynamic data in infinitesimal concentration is a measure of the selectivity of counter ions in the trace amounts of the ion exchanger.

Equilibrium studies on ion exchange materials have been performed by several workers. Amphlett and McDonald[14] have studied the ion exchange equilibria

of NH_4^+, Na^+, Cs^+ and Sr^{2+} on clay mineral fraction of a soil from the English Lower Greensand series at 20°C. Ion exchange equilibria of Fe^{2+} on Na^+- montmorillonite have been studied by Singhal et al.[101] Ion exchange equilibria of NH_4^+, Ag^+ and alkali and alkaline earth metal ions on natural and synthetic zeolites have been extensively studied.[48,102-106] Equilibrium studies on zirconium phosphate have been reported to a greater extent. The ion exchange equilibria of Li^+, Na^+, K^+ and Cs^+ was studied by Larsen and Vissars[107] and Gal and Ruvarac[108] on amorphous zirconium phosphate of various composition and properties. Some admirable studies on ion exchange thermodynamics of alkali metal ions have been made with more defined simicrystalline and crystalline zirconium phosphate.[109-119] The thermodynamic parameters have been interpreted in terms of the nature of bonding between alkali metal ions and the matrix of the exchanger, zirconium phosphate. Larsen and Cilly[120] made equilibrium studies on cerium phosphate. Baetsle[121] studied the ion exchange equilibria of Cs^+, Rb^+, Ca^{2+}, Sr^{2+}, Eu^{3+} and Ce^{3+} ions with hydrogen ion on zirconium phosphate, both at micro and macro concentration levels over a range of temperature from 5 to 71°C. The ion exchange equilibria of Ca^{2+} - H^+[122]

and UO_2^+ - H^+[123] exchange on crystalline zirconium phosphate have been studied by Ruvarac. Ceramic and Adomovic[124] studied the ion exchange equilibria on cobalt (II) hexacyanoferrate. Recently ion exchange equilibrium studies of alkali metals with hydrogen ion have been carried out on tin antimonate[125] and antimonic acid[126,143-147]. M. Abe[125] reported the hypothetical thermodynamic data on "zero loading" on the ion exchange reaction and has calculated various other thermodynamic parameters. Thermodynamic treatment of exchange of alkali metals with hydrogen ion on α and γ titanium phosphate has also been carried out.[127-129] The thermodynamic studies of alkali and alkaline earth metal ions on ferric antimonate[130,131] and niobium arsenate[132] were made in our laboratories.

Some equilibrium studies on different ion exchange materials with systems and various parameters are given in Table I.2.

The thermodynamics of anion exchange on the ion exchange materials have also been studied. The reversibility of Br^-- NO_3^- exchange on hydrous zirconia was demonstrated by Kraus.[148] Ruvarac[149] studied the thermodynamics of Cl^- and SO_4^{2-} from solution on NO_3^- form of hydrous zirconia at 25-80°C. The thermodynamics

TABLE - I.2

Equilibrium studies on aluminosilicates and other inorganic ion exchangers

Serial No.	Ion exchange material	Systems studied	Various parameters	References
	I- ALUMINOSILICATES			
1.	Lower greensand soil (clay fraction)	Na^+-Cs^+, NH_4^+-Cs^+ and Sr^{2+}-Cs^+ exchange	K, $\Delta G°$ and $\Delta H°$	14
2.	Montmorillonite	K^+-Cs^+, Sr^{2+}-Cs^+ and Y^{3+}-Cs^+ exchange	K, $\Delta G°$ and $\Delta H°$	133,134
3.	Montmorillonite	Fe^{2+}-Na^+ exchange	Exchange isotherm K, $\Delta G°$, $\Delta H°$ and $\Delta S°$	101
4.	Linde Sieve 4A	Ag^+-Na^+, Tl^+-Na^+ and Na^+-Ag^+ exchange	Exchange isotherms, $\Delta G°$, $\Delta H°$, $\Delta S°$ and Kielland coefficient	102
5.	Chabazite	Ag^+-Na^+, K^+-Na^+, Rb^+-Cs^+, Tl^+-Na^+ and Na^+-Ag^+	K, $\Delta G°$, $\Delta H°$ and affinity series $Na^+ < Ag^+ \leqslant Rb^+ < K^+ < Tl^+$	103
6.	Basic sodalite	Li^+-Na^+, K^+-Na^+ and Ag^+-Na^+	Exchange isotherms and selectivity $Ag^+ \gg Na^+ > Li^+ > K^+$	48

Contd...

Serial No.	Ion exchange material	Systems studied	Various parameters	References
7.	Basic cancrinite	Li^+-Na^+	Exchange isotherms and Kielland coefficient	48
8.	Analcite	K^+-Rb^+ and Rb^+-K^+	Forward and reverse exchange isotherms	48
9.	Mineral clinoptilolite	Cs^+-Na^+	Selectivity, K and $\Delta G°$	104
10.	Ferriate	Na^+, K^+, Rb^+, Cs^+, Sr^{2+}, Ca^{2+}, Ba^{2+}, NH_4^+ and Ag^+	$\Delta H°$	106
	II- ZIRCONIUM PHOSPHATE			
1.	Crystalline zirconium phosphate	Na^+-K^+, Na^+-Li^+, K^+-Li^+ and Na^+-Cs^+	Exchange isotherm and selectivity $K^+ > Cs^+ > Na^+ > Li^+$	135
2.	-do-	Cs^+-H^+ and Rb^+-H^+	Forward and reverse exchange isotherms, X-ray differactogram	136
3.	Semicrystalline zirconium phosphate	Li-H^+, K^+-H^+ and Cs^+-H^+	$\Delta G°$, $\Delta H°$ and $\Delta S°$	110
4.	-do-	Cs^+-Rb^+ and Cs^+-K^+	K, $\Delta G°$ and $\Delta H°$	109
5.	-do-	Cs^+-H^+ and H^+-Cs^+	K	111

Contd...

Serial No.	Ion exchange material	Systems studied	Various parameters	References
6.	Zirconium phosphate	UO_2^+-H^+	K, ΔG, ΔH and ΔS	123
7.	Crystalline α zirconium phosphate	Na^+-H^+ and Cs^+-H^+	Phase formed during the exchange at equilibrium	137
8.	α zirconium phosphate	K^+-H^+	$\Delta G°$, $\Delta H°$ and $\Delta S°$	138
9.	-do-	Na^+-H^+	K, ΔG, ΔH and ΔS	139
10.	-do-	Li^+-H^+, Na^+-H^+ and K^+-H^+	Exchange isotherms and X-ray analysis	112
11.	-do-	Li^+-H^+, Na^+-H^+, K^+-H^+, Ca^{2+}-H^+ and Sr^{2+}-H^+	Equilibrium and kinetic studies, X-ray photographs	140
12.	-do-	K^+-H^+	Complete layer structure	141
13.	-do-	Li^+-Cs^+, Na^+-Cs^+ and K^+-Cs^+	K, $\Delta G°$ and $\Delta H°$	142
14.	-do-	Cs^+-H^+	$\Delta G°$ (298°K)	111

Contd...

Serial No.	Ion exchange material	Systems studied	Various parameters	References
	III- OTHERS			
1.	Crystalline antimonic acid	Mn^{2+}-H^+, Co^{2+}-H^+, Ni^{2+}-H^+, Cu^{2+}-H^+, Zn^{2+}-H^+ and Ca^{2+}-H^+	ln K, ΔG, ΔH and ΔS	143
2.	-do-	Mg^{2+}-H^+, Ca^{2+}-H^+, Sr^{2+}-H^+ and Ba^{2+}-H^+	Selectivity, reversibility, X-ray studies	144
3.	-do-	Mg^{2+}-H^+, Sr^{2+}-H^+, Ca^{2+}-H^+, Ba^{2+}-H^+ and Pb^{2+}-H^+	Kielland coefficient, $(\ln K_H^M)_{\bar{x}_M} \rightarrow O$	145
4.	-do-	Li^+-H^+, Na^+-H^+, K^+-H, Rb^+-H^+ and Cs^+-H^+	ln K, ΔG and X-ray studies	146
5.	-do-	NH_4^+-H^+, $CH_3NH_3^+$-H^+, $C_2H_5NH_3^+$-H^+, $(CH_3)_2NH^+$-H^+, iso $C_3H_7NH_3^+$-H^+ and $(C_2H_5)_4\ N^+$-H^+	ln K, ΔG, ΔH and ΔS	147
6.	Cerium phosphate	Li^+-H^+, Na^+-H^+ and K^+-H^+	ΔH°	120
7.	Ferric antimonate	Li^+-H^+, Na^+-H^+, K^+-$H^+$and Rb^+-H^+	K, ΔG°, ΔH° and ΔS	131

Contd...

Serial No.	Ion exchange material	Systems studied	Various parameters	References
8.	Ferric antimonate	Ba^{2+}-Na^{+}, Mg^{2+}-Na^{2+}, Ca^{2+}-Na^{+} and Sr^{2+}-Na^{+}	K, $\Delta G°$, $\Delta H°$ and $\Delta S°$	130
9.	Niobium arsenate	Na^{+}-H^{+}, K^{+}-H^{+}, Mg^{2+}-H^{+}, Ca^{2+}-H^{+}, Sr^{2+}-H^{+} and Ba^{2+}-H^{+}	K_H^M, ΔG, $\Delta H°$, ΔS and ΔS_{Ex}	132
10.	γ titanium phosphate	K^{+}-H^{+} and Na^{+}-H^{+}	K, ΔG and ΔH	128,129
11.	*Tin antimonate*	Li^{+}-H^{+}, Na^{+}-H^{+}, K^{+}-H^{+}, Rb^{+}-H^{+} and Cs^{+}-H^{+}	$(ln\ K_H^M)_{\bar{x}_M} \rightarrow 0$ and selectivity $Na^{+} < K^{+} < Rb^{+} < Cs^{+} \ll Li^{+}$	125

of Cl^- - NO_3^-, Cl^- - SCN^- and SCN^- - NO_3^- exchange on hydrous zirconium oxide was studied by Nancollas and Paterson.[150] Recently, similar studies have been made for the exchange of $Cr_2O_7^{2-}$, CrO_4^{2-}, SO_4^{2-}, $S_2O_3^{2-}$ and MnO_4^- on zerconium bis - triethylamine at 30-60°C.[151]

Although, the thermodynamics is a useful means for investigating the conditions at equilibrium; it does not give any information about the mechanism of ion exchange process and the time required for the change of one state to the other. For this purpose kinetic studies are performed which explain these factors well.

The kinetics is a time-dependant study. The rate of the reaction governs the kinetics of simple homogeneous reactions which depends upon the concentration of the reactants. However, ion exchange is diffirent from such chemical reactions. Ion exchangers are in solid phase and thus constitute a different phase than the solution phase. Hence, ion exchange is a heterogeneous process; it involves the diffusion of counter ions from solution to the exchanger (solid) phase and vice versa. Furthermore, in ion exchange the co-ions do not take part in the overall reaction mechanism. It is a stoichiometric process and electroneutrality

is preserved throughout the process in both the phases. To understand the kinetics of ion exchange we consider a spherical bead particle of the ion exchanger placed in a solution of counter ions. Sculze[152] recognised that rate determining step in ion exchange is inter-diffusion of counter ions rather than a chemical exchange reaction between the two counter ions. The first serious attempt on the ion exchange kinetics was made by Nachod and Wood.[153] They studied the rate at which counter ions are removed from solution by the ion exchanger and conversely, the rate at which exchangeable ions are released into the solution by the ion exchanger. Later on, Boyd et al.[154] studied the ion exchange kinetics by considering the ion exchanger beads surrounded by a thin liquid film called Nernst diffusion layer. They gave an elaborate model to understand the inter-diffusion of counter ions in the film and within the ion exchanger bead. Thus ion exchange kinetics involves three types of processes.

1. Interdiffusion of counter ions in the adherent film - "film diffusion"
2. Interdiffusion of counter ions within the exchanger bead particle - "particle diffusion"
3. Chemical exchange reaction between the two counter ions.

Of all the kinetic studies reported in literature to date, none has shown ion exchange process being governed by the chemical exchange reaction between the two counter ions, as recognised earlier by Sculze.[152] Thus in ion exchange the rate determining step may be either particle diffusion or film diffusion depending upon the physical and chemical parameters.[155] The slower of the two will determine the rate of ion exchange process. In intermediate cases the rate of ion exchange may be affected by both the steps. Reicenberg[156] confirmed that at high concentration the rate is independent of the ingoing ions while at low concentration the reverse is true. Apart from concentration several other factors also determine the nature of rate controlling step. The best technique for distinguishing between particle and film diffusion control is an experimental method called "interruption test".[157] Nancollas[158] studied the kinetics of Na^+ - H^+ exchange on crystalline zirconium phosphate. The self diffusion process of Na^+ and K^+ on microcrystals of $Zr(NaPO_4)_2.3H_2O$ and $Zr(KPO_4)_2.3H_2O$ and modified Ficks equation to account for the nonuniformity of the particle size have been studied by Costantino et al.[159]. Barrer studied the kinetics of ion exchange on different zeolites and organic resins.[160,161] Recently ion exchange

kinetics on tantalum arsenate[162], iron antimonate[163], stannic arsenate[164], sodium dickite[165] and zirconium bis- triethylamine[166] have been studied in our laboratories.

The ion exchange materials have found a number of important analytical applications. An introductory description on the application of natural and synthetic ion exchangers has been given by Kuroda.[167] The analytical applications of ion exchange continue to increase at an exponential rate. Newer and newer areas of application are actively being sought day after day. Ion exchange has found its application in -

1. Water pollution control - purification of water
2. Removal of interfering ions
3. Recovery of precious metals
4. Preparation of deionized water
5. Water softening
6. Determination of total salt content of a solution
7. Separation of metal ions
8. Separation of organic and biologically important substances
9. Concentration of trace constituents
10. Specific spot tests
11. Location of end point in titrations

12. Gas chromatography, electrophoresis and solid state separations
13. Preparation of ion selective electrodes, and
14. Preparation of ion exchanger fuel cells.

The most important application of ion exchangers is purification of water. The water pollution is increasing day by day due to increase in industrialization and urbanization. In its natural state water always contains dissolved impurities. Organic matters and suspended solids are more hazardous than minerals. Ion exchange technology is useful for removing these toxic species, when present in ionic form. The great simplicity of the technique makes ion exchange very attractive and inexpensive tool for this purpose. Purification on large scale can be made by passing the sample solution through the ion exchanger bed which takes up certain materials in preference of others.

The removal of one or more interfering ions by replacement with an innocuous ion is an obvious application of ion exchange. This technique can also be utilized to recover traces of useful elements from dilute solutions. The elements present in ionic form are exchanged by an equivalent amount of counter ion present in the exchanger

and subsequently eluted from the exchanger by suitable electrolytic reagents. Thus, a trace amount of an ion is isolated or concentrated from a large volume of aqueous solution into a small volume of the eluent. This is a common step in the determination of trace metals in water, copper in milk[168] or the recovery of precious metals. This technique has been used for the isolation and identification of the new trans uranium elements[169-173] and for the enrichment of isotopes[174-177].

Water softening is perhaps the most common application of ion exchange. Calcium, magnesium, iron and several other charged cations are replaced by sodium, when hard water is passed through a column of sodium form ion exchanger. The softened water then contains sodium salts which are innocuous for most of the uses. Sodium is chosen because it is harmless in water and because the ion exchanger can be easily regenerated by using a saturated solution of common salt.

Completely deionized water is prepared by passing the raw water through a cation exchanger which replaces all cations with hydrogen ion and then through an anion exchanger which replaces all anions with hydroxide ion. In effect, the salts are replaced with the ions of water.

The two exchangers can be combined in a single mixed bed so that the water never becomes too acidic or basic as it might if passed through the two ion exchangers separately. The determination of total salt content of a solution is considerably simplified by conversion of the cations to hydrogen ion or the anions to hydroxide ion, followed by simple acid base titration.

Ion exchange being a concentration and separation technique finds its use in water analysis to concentrate the trace quantities and separate[178,179] one substance from the other. Ion exchange is especially advantageous for the separation of metal ions with similar properties for which specific methods are not available. For example alkali and alkaline earth metals are always difficult to determine in a mixture, but can be readily separated in an ion exchange column. Ion exchangers have been used to solve previously unsolvable problems such as the separation of rare earths.[180-185] Taylor and Urey have performed partial separation of lithium isotopes[186]. Ion exchange columns now provide pure rare earth compounds on commercial scale.

The versatility of ion exchange methods has been proved by achieving the separation of organic and biologically important substances. The most impressive

example is the separation of the complex mixtures of aminoacids[187-195]. Various other substances such as peptides[196,197], proteins[198], nucleic acids[199], carbohydrates and their derivatives[200-204], alcohols[205-206], glycols[207-208], carbonyl compounds[209,210], ethers[211], amines[212,21], hydrocarbons[214] and phenols[215] have also been separated on ion exchange columns.

Ion exchangers are also useful in gas chromatography, solid state separations, electrophoresis, location of end point in titrations, specific spot tests and preparation of ion selective electrodes[216-219]. Papers impregnated with ion exchangers are used for chromatographic separations.

A recent application of ion exchangers has emerged as their use in the preparation of fuel cells. Ion exchanger fuel cells have many advantages over others such as their low cost, pollution free operation, regenerative nature and easy reaction conditions. In these fuel cells chemical energy is directly converted into electrical energy. Heat is not involved in the conversion process and a high conversion efficiency is possible. However, very few literature is available on the ion exchanger fuel cells. A cation exchange membrane electrolyte has been used by Fugita et al.[220] for the

preparation of a fuel cell. Mucoyama et al.[221] used a strongly acid cation exchange resin for this purpose. A fibrous ion exchanger sheet has also been used for the preparation of the fuel cells[222]. Kummer and Oei[223] prepared a chemically regenerable redox fuel cell using a cation exchange membrane. Zirconium phosphate membrane impregnated with a catalyst has been used by Berger and Strier which can perform in a fuel cell at 0.77-0.78 V.

In the present work an analogue of the zeolites, sodium stannosilicate has been synthesized. Its physical and chemical properties have been studied and its applicability to the separation and recovery of metal ions have been highlighted. Detailed thermodynamic studies have also been carried out on the above mentioned ion exchanger. Sorption equilibria of lead(II) on two Indian soils, the natural ion exchangers, have been studied and various thermodynamic parameters are evaluated. The application of organic ion exchange resins has been described for the production of electrical energy by preparing a redox ion exchanger fuel cell. The use of the redox ion exchanger fuel cell is demonstrated with the help of a simple equipment.

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Chapter II

Synthesis and Ion Exchange Properties of Sodium Stannosilicate: A Silver Selective Inorganic Ion Exchanger

II.1 INTRODUCTION

The use of synthetic inorganic ion exchangers is successfully being developed for selective separation of metal ions and recovery of precious metals. New materials are being synthesized[1-4] to solve such specific problems. There is a revived interest towards the ion exchange properties of silicates[5-9]. Desai and Baxi[6] have synthesized tin silicate and studied their ion exchange properties. Zeolites are aluminosilicate minerals with ion exchange properties. They are characteristic representative of most of the natural ion exchange materials. Natural and synthetic zeolites have been extensively studied[10-18], particularly by Barrer[10-15], for their ion exchange properties. Various zeolites, with completely regular structure, have been synthesized by several workers[11,12,17,18]. Recently ion exchange behaviour of ferriate has been studied by Dyer and Ahmad[19]. The analogues of the zeolites have been prepared by replacing silicon with other tetravalent elements and aluminium with other trivalent elements. Several analogues of the zeolites such as aluminogermanate[20], sodium gallosilicate[21], gallocarbonate[22], ammonium tungstosilicate[23] and other metallosilicates[24] have been synthesized for comparison with the zeolites. Recently ferrosilicate[25] was synthesized

by Lok and Messina.

The present paper reports the synthesis, chemical composition, chemical and thermal stabilities and ion exchange properties of sodium stannosilicate, an analogue of the zeolites. This material shows higher exchange capacity and is more stable at high temperatures than tin silicate[6] prepared at pH 8.5. The distribution ratios for different metal ions have revealed that the exchanger is specific towards Ag^+. K_d values for other metal ions are also higher for sodium stannosilicate than those for tin silicate. The utility of this material has been studied for the separation of Ag^+ from other metal ions and its recovery from dilute solutions.

II.2 EXPERIMENTAL

II.2.1 Reagents: Tin(IV) chloride pentahydrate($SnCl_4 . 5H_2O$) (Reachim) and sodium metasilicate($Na_2SiO_3 . 5H_2O$) (Loba) were used. All other chemicals used were of A.R. grade.

II.2.2 Apparatus: An electric temperature controlled SICO shaker and Bausch and Lomb sepctronic-20 (U.S.A.) were used for shaking and spectrophotometric determinations respectively. Elico pH meter model Li-10 (India) was used for pH measurements.

II.2.3 Preparation of sodium stannate solution: Sodium stannate ($Na_2SnO_3 . 3H_2O$) was prepared by mixing 0.5 M sodium hydroxide solution to 0.1 M tin(IV) chloride solution.[26] The pH was adjusted to 10 by adding sodium hydroxide solution. The solution initially turbid, turned into a clear solution of sodium stannate on heating at 60±1°C.

II.2.4 Synthesis of sodium stannosilicate: Sodium stannosilicate was synthesized by mixing 0.1 M sodium metasilicate solution with 0.1 M sodium stannate solution in 1:1 volume ratio (Table II.1). Any alteration in the ratio of the reagents either resulted in the disappearence of the precipitate or the yield was less. Therefore 1:1 volume

ratio was chosen for synthesis. The resulting mixture was refluxed for 24 hours. The white precipitate so obtained was allowed to settle overnight, washed with distilled water and dried at 60±1°C. The dried product was immersed in distilled water when it broke down easily into small granules. It was washed several times with distilled water and then dried in an air oven at 60±1°C.

TABLE - II.1

Conditions of preparation and properties of sodium stannosilicate

Sample	Molarity of reagents		Mixing volume ratio	Properties	
	Sodium stannate	Sodium metasilicate		Nature of precipitate	Ion exchange capacity for Ag^{+} ($meq\ g^{-1}$)
S_1	0.1	0.1	1:1	A thick white precipitate	2.25
S_2	0.1	0.1	1:2	Mild precipitate	-
S_3	0.1	0.1	2:1	Mild precipitate	-
S_4	0.1	0.1	1:3	No precipitate	-
S_5	0.1	0.1	3:1	No precipitate	-

II.3 RESULTS

II.3.1 Cation Exchange Capacity: Ion exchange capacity for H^+ ion was determined by taking sodium stannosilicate in H^+ form and then eluting with 1.0 M sodium nitrate solution. The H^+ ions liberated in the effluent were titrated with 0.1 M NaOH solution. Metal ion capacity was determined by shaking 1.0 g of the exchanger with 50 ml 0.1 M aqueous solution of metal nitrate at 25±1°C and titrating the metal ion left in the supernatant liquid with 0.02 M EDTA solution. The results are given in Table II.2.

TABLE - II.2

Cation exchange capacity of sodium stannosilicate

Serial No.	Cation	Exchange capacity (meq g^{-1})
1	H^+	0.23
2	Ag^+	2.25
3	Mg^{2+}	0.80
4	Ca^{2+}	1.00
5	Cu^{2+}	1.20
6	Co^{2+}	0.90
7	Mn^{2+}	1.00
8	Hg^{2+}	1.44
9	Pb^{2+}	1.20
10	Cd^{2+}	1.10

II.3.2 Chemical Stability: The chemical stability of sodium stannosilicate was studied in different solvents. For this purpose 100 mg of the exchanger was shaken with 25 ml of the appropriate solvent for 6 hours at 25±1°C. The amount of silica released in the supernatant liquid was determined by a standard colorimetric method[27]. The results are given in Table II.3.

TABLE - II.3

Chemical stability of sodium stannosilicate in different solvents

Amount of sodium stannosilicate taken = 100 mg

Serial No.	Solvents	Amount of silica released (mg/25 ml)
1	Distilled Water	0.000
2	Nitric acid, 0.1 M	0.127
3	Hydrochloric acid, 0.1 M	0.127
4	Sulfuric acid, 0.1 M	0.165
5	Ethanol	0.000
6	Sodium acetate, 1 M	0.000
7	Sodium hydroxide, 0.1 M	0.185
8	Sodium nitrate, 1 M	0.000
9	Sodium citrate, 1 M	0.000

II.3.3 Chemical Composition: A 200 mg portion of sodium stannosilicate was dissolved in 200 ml solution containing 15 ml of sulfuric acid and 100 ml of hydrochloric acid. Tin in this sample was reduced by zinc powder and determined iodometrically.[28] For the determination of silicon a 200 mg portion of the exchanger was heated in 200 ml solution containing 100 ml of hydrochloric acid. Silicon was precipitated as silicic acid. It was ignited in a platinum crucible and weighed as SiO_2.[29] The apparent ratio of Sn:Si was found to be 1:1.

II.3.4 Thermal Stability: Sodium stannosilicate (0.5 g) was weighed in different silica crucibles and dried at different temperatures in a muffle furnace for 2 hours. Exchange capacity for Ag^+ was determined for the products dried at 60, 100, 150, 200 and 250°C. Weight loss was also calculated at the respective temperatures. The results are presented in Table II.4 and plotted in Figure II.1.

II.3.5 Hydrolysis: Sodium stannosilicate was taken in H^+ and Na^+ forms. The exchanger (0.5 g) was shaked with 25 ml of distilled water at 25±1°C for different time intervals. The pH of the supernatant liquid was measured after each time-interval. The results are given in Table II.5 and plotted in Figure II.2.

TABLE - II.4

Capacity and weight loss of sodium stannosilicate dried at different temperatures

Serial No.	Temperature (°C)	% weight loss	Capacity for Ag^+ (meq g^{-1})
1	60	0.00	2.25
2	100	3.70	2.25
3	150	8.12	2.24
4	200	8.32	2.24
5	250	8.36	2.24

TABLE - II.5

Hydrolysis of sodium stannosilicate in H^+ and Na^+ form at different time intervals

Initial pH of distilled water = 6.80

Serial No.	Time (minutes)	pH	
		H^+ form sodium Stannosilicate	Na^+ form sodium stannosilicate
1	5	6.10	8.40
2	10	5.90	8.80
3	15	5.80	9.30
4	20	5.75	9.50
5	30	5.80	9.80
6	40	5.80	9.75
7	50	5.80	9.75
8	60	5.80	9.75
9	70	5.80	9.75
10	80	5.75	9.75
11	90	5.80	9.80
12	100	5.80	9.75

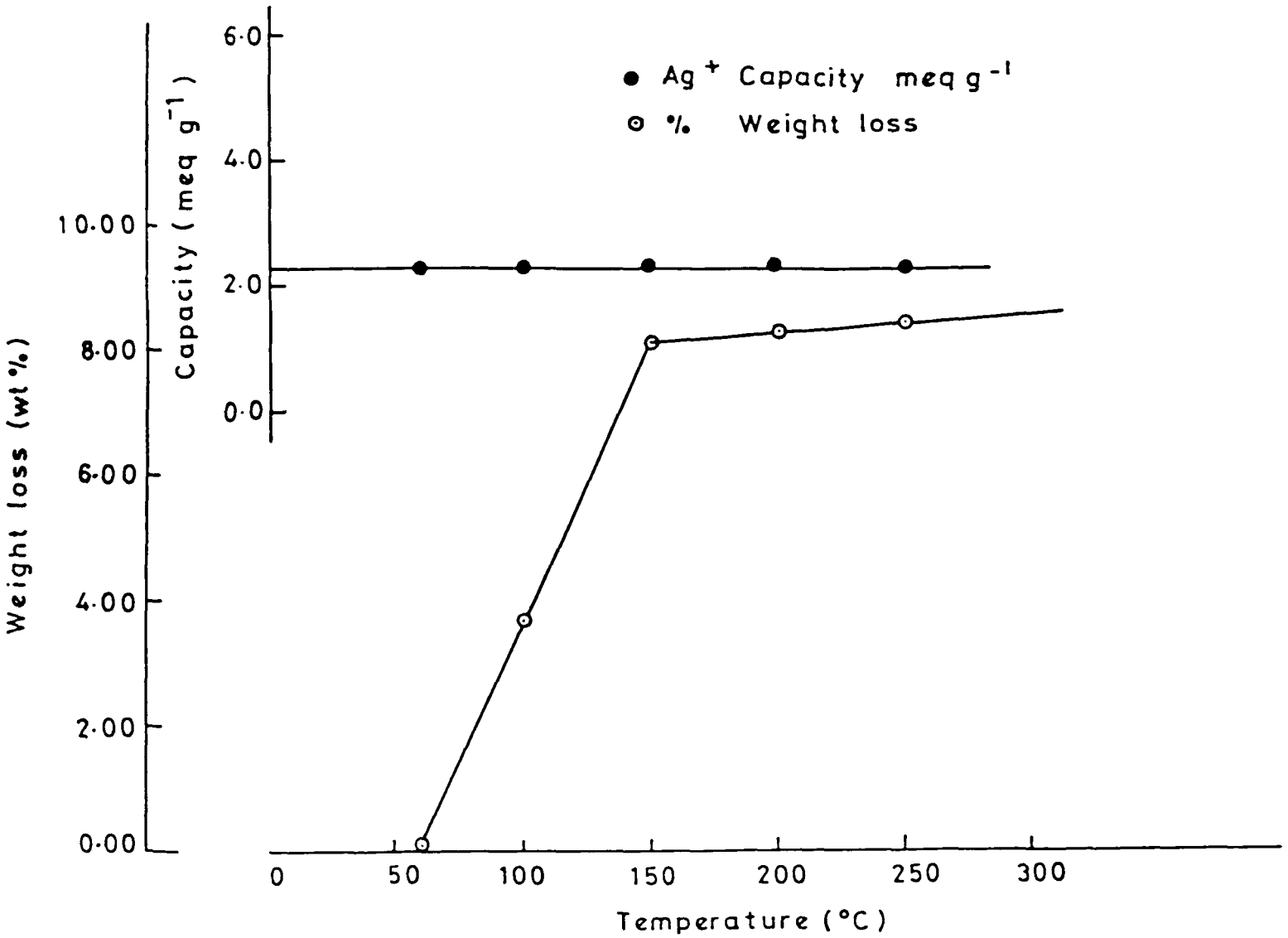

Figure II.1 Capacity and weight loss of sodium stannosilicate at different temperatures

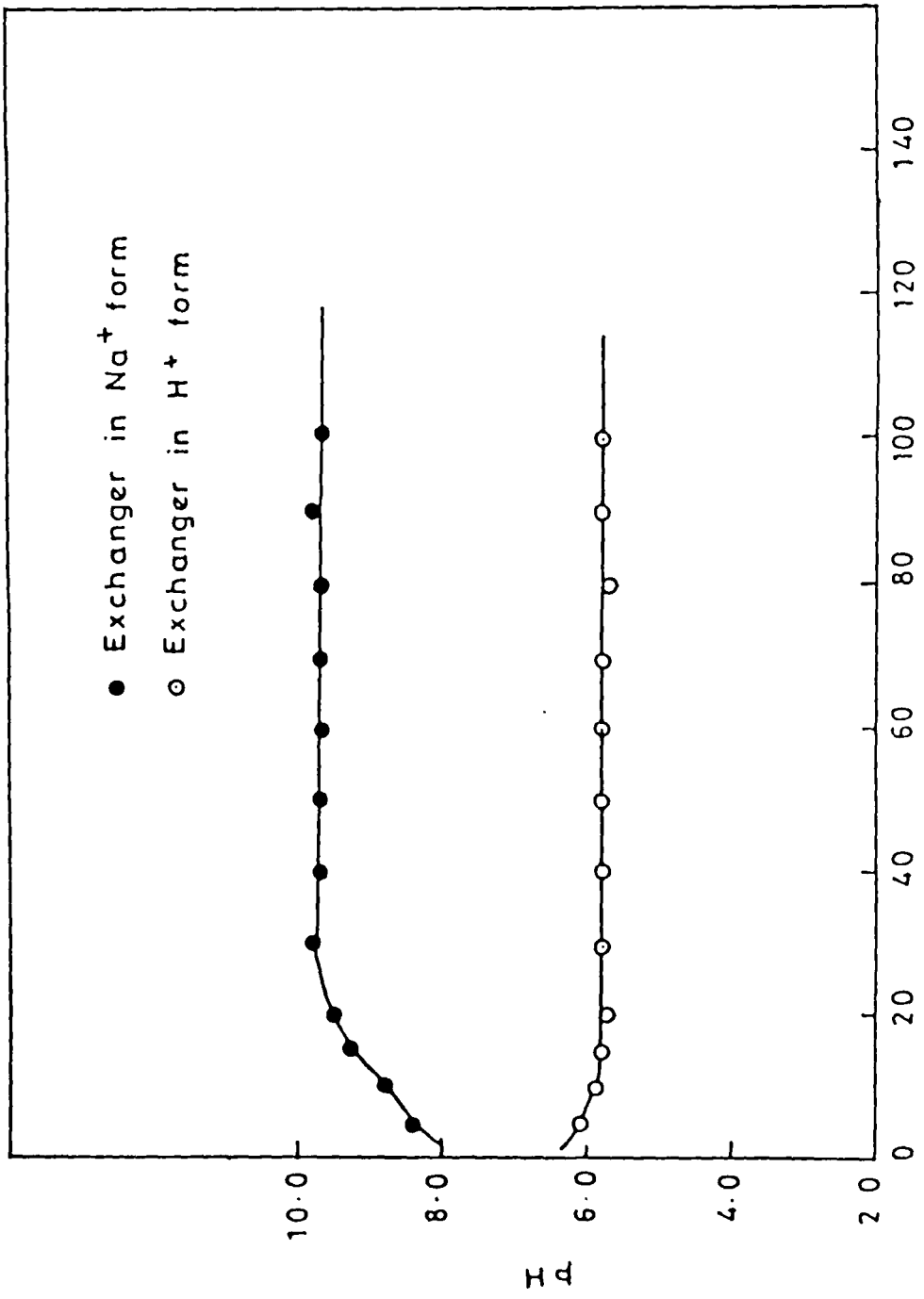

Figure II.2 Hydrolysis curves of sodium stannosilicate

II.3.6 Water Sorption: Sodium stannosilicate (1.0 g) in different ionic forms was equilibrated with 20 ml of distilled water for 1 hour at 25±1°C. Sodium stannosilicate was then separated from water and weighed in a stoppered weighing bottle. It was then dried over a dessicant in vacuum at 60±1°C and reweighed. Amount of water sorbed by sodium stannosilicate was calculated from the difference between the wet weight and dry weight. The results are summarized in Table II.6.

TABLE - II.6

Water sorption on sodium stannosilicate in different ionic forms

Serial No.	Counter ion	Ionic radius (A°)	Water sorbed (g/g)
1	Li^+	0.68	0.4910
2	Na^+	0.98	0.4700
3	K^+	1.33	0.4154
4	Rb^+	1.49	0.3240

II.3.7 IR Analysis: IR-spectrum of the material dried at 60±1°C was obtained using KBr disc technique on an IR-20 spectrometer. Figure II.3 shows the spectrum of the material.

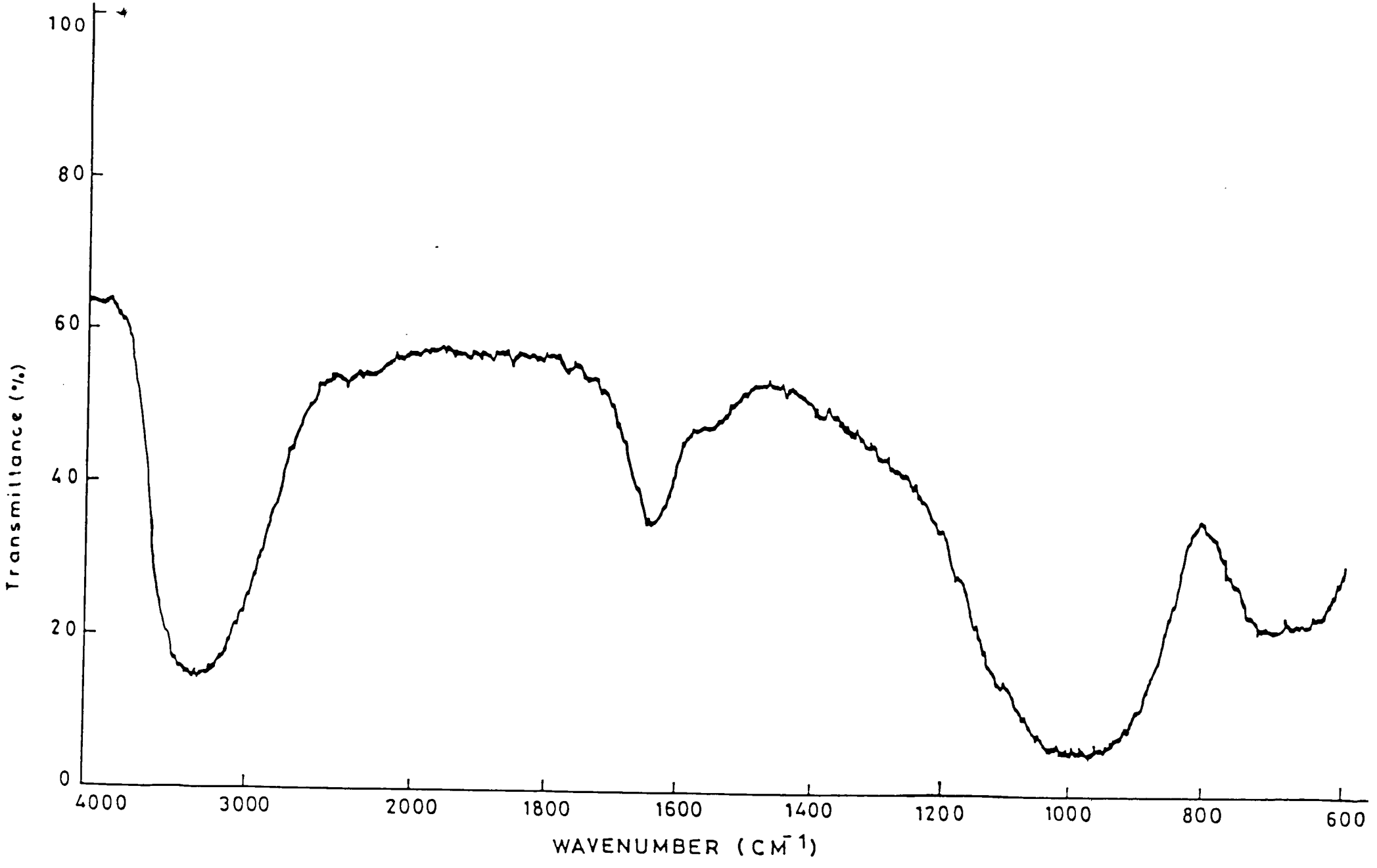

Figure II.3 IR - spectrum of sodium stannosilicate

II.3.8 Distribution Coefficients: Sodium stannosilicate (0.5 g) was shaken with 50 ml of 0.02 M solution of the metal nitrate for 6 hours at 25±1°C. The supernatant liquid was titrated for the determination of metal ion left. Silver was determined by titration with 0.02 M KSCN solution. All other cations were determined by titration with 0.02 M solution of EDTA. The K_d values of these ions were determined in aqueous solution. The results are summarized in Table II.7.

TABLE - II.7

K_d values for some metal ions on sodium stannosilicate

Serial No.	Metal ion	K_d values (ml g^{-1})	Serial No.	Metal ion	K_d values (ml g^{-1})
1	Fe^{3+}	33.33	8	Cu^{2+}	109.09
2	Mg^{2+}	57.14	9	Cd^{2+}	110.00
3	Ni^{2+}	61.54	10	Pb^{2+}	133.33
4	Co^{2+}	75.00	11	Al^{3+}	200.00
5	Ba^{2+}	75.00	12	Hg^{2+}	400.00
6	Mn^{2+}	83.33	13	Ag^{2+}	3400.00
7	Sr^{2+}	90.91	14	Ca^{2+}	90.91

Distribution coefficient values for a number of metal ions on sodium stannosilicate were calcutated from the relationship

$$K_d = \frac{I - F}{F} \times \frac{V}{W}$$

Where I and F are initial and final volumes of titrant before and after equilibration. V is volume of the metal ion solution and W the weight of the exchanger.

II.3.9 Column Separations: A glass column (length 45 cm, diameter 0.39 cm) was filled to a height of 14 cm with 2.0 g of the exchanger on a glass wool support. The column was washed with 10 bed volumes of distilled water. The aqueous mixture solution (10 ml) containing the metal ions to be separated was passed onto the column at a slow rate. The column was again washed with distilled water. The metal ions retained by the exchanger were then eluted by passing a suitable eluent. The eluent was passed at a flow rate of 0.2 ml min^{-1}. The metal ions in 10 ml fractions of effluent were collected and determined titrimetrically. Table II.8 shows a list of quantitative separations achieved on a column of sodium stannosilicate. The order and the eluents are presented in Figures II.4, II.5 and II.6.

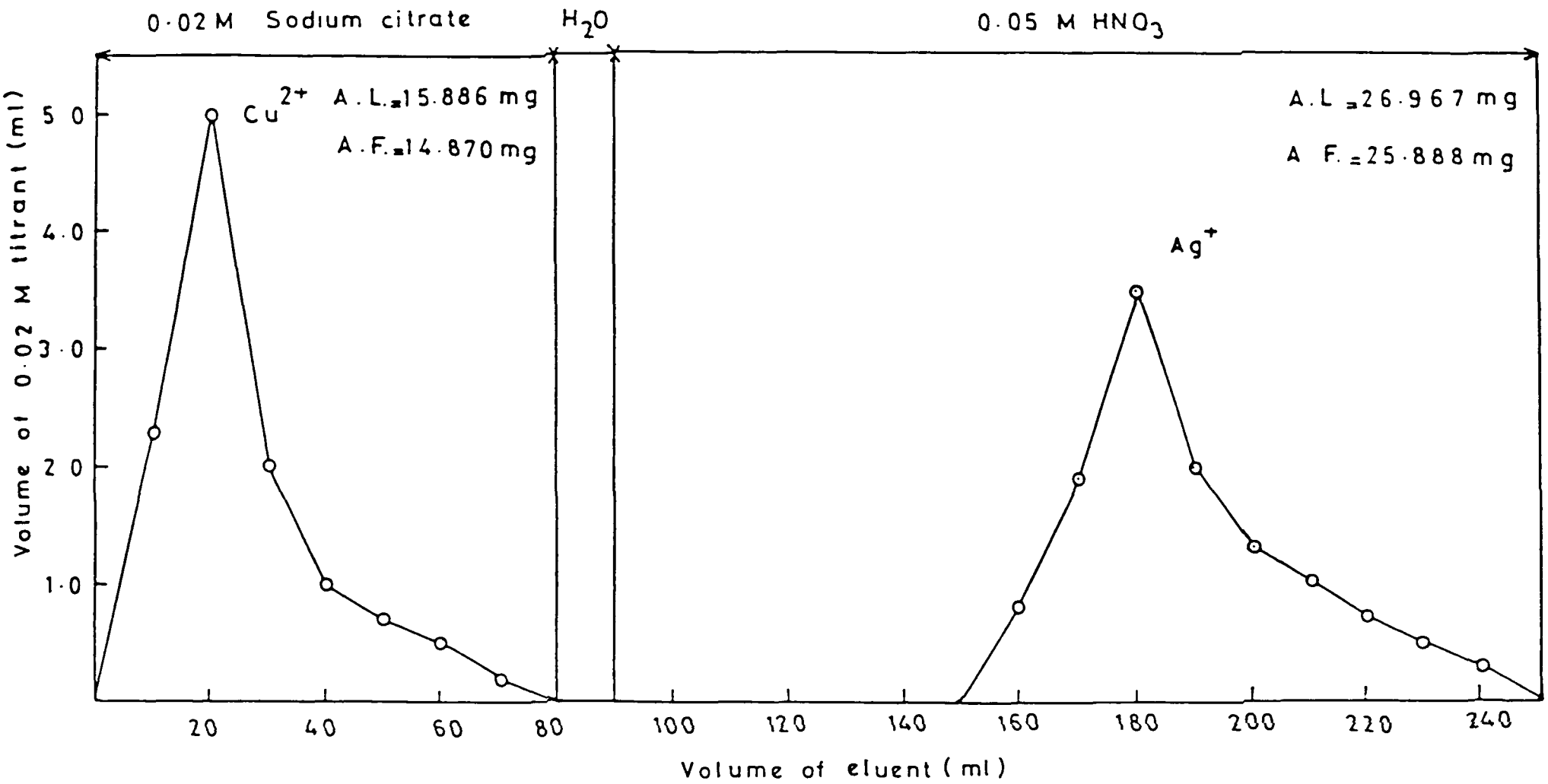

Figure II.4 Separation of Ag^+-Cu^{2+} on sodium stannosilicate column

A.L. = Amound loaded, A.F = Amount found

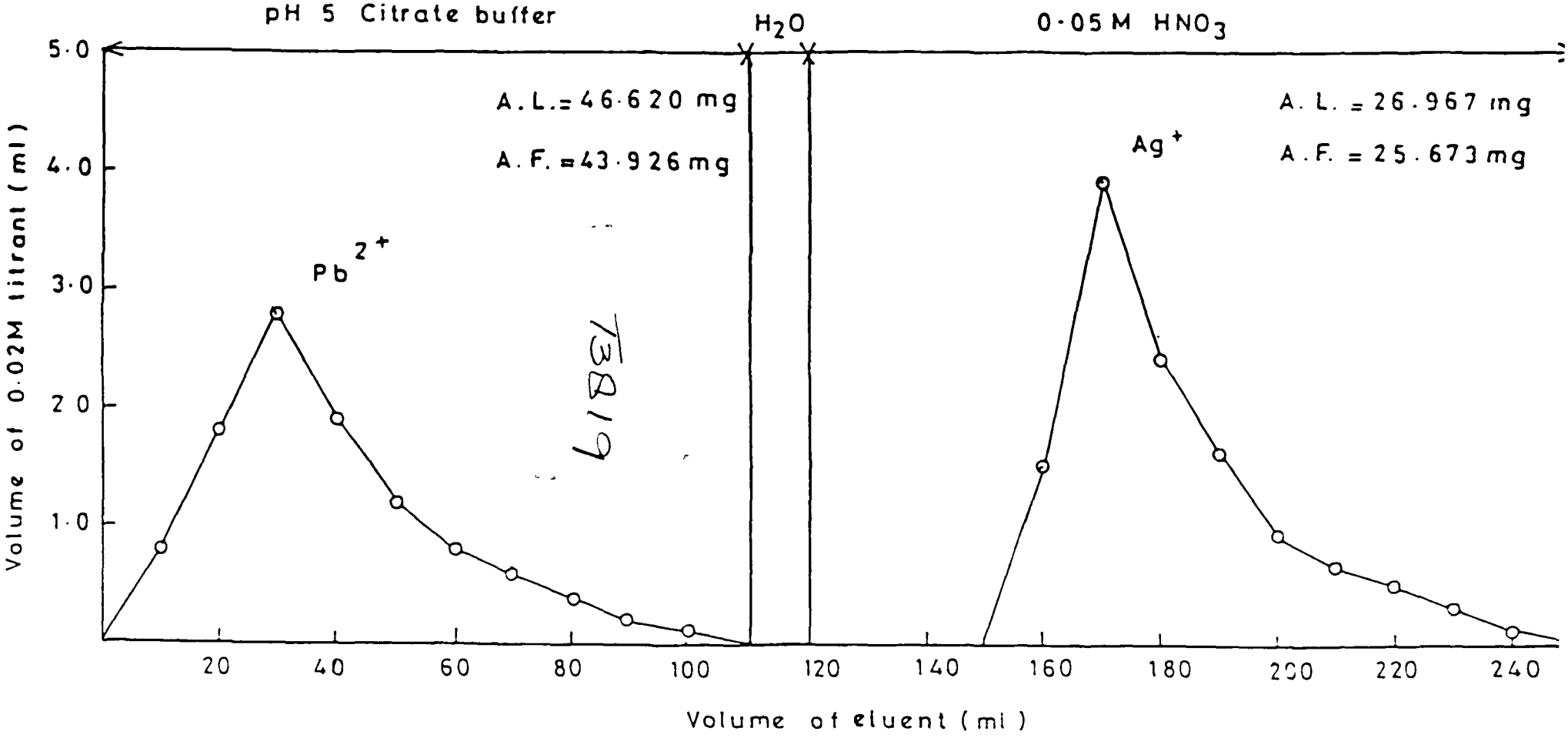

Figure II.5 Separation of Ag^+-Pb^{2+} on sodium stannosilicate column

A L.= Amount loaded, A F = Amount found

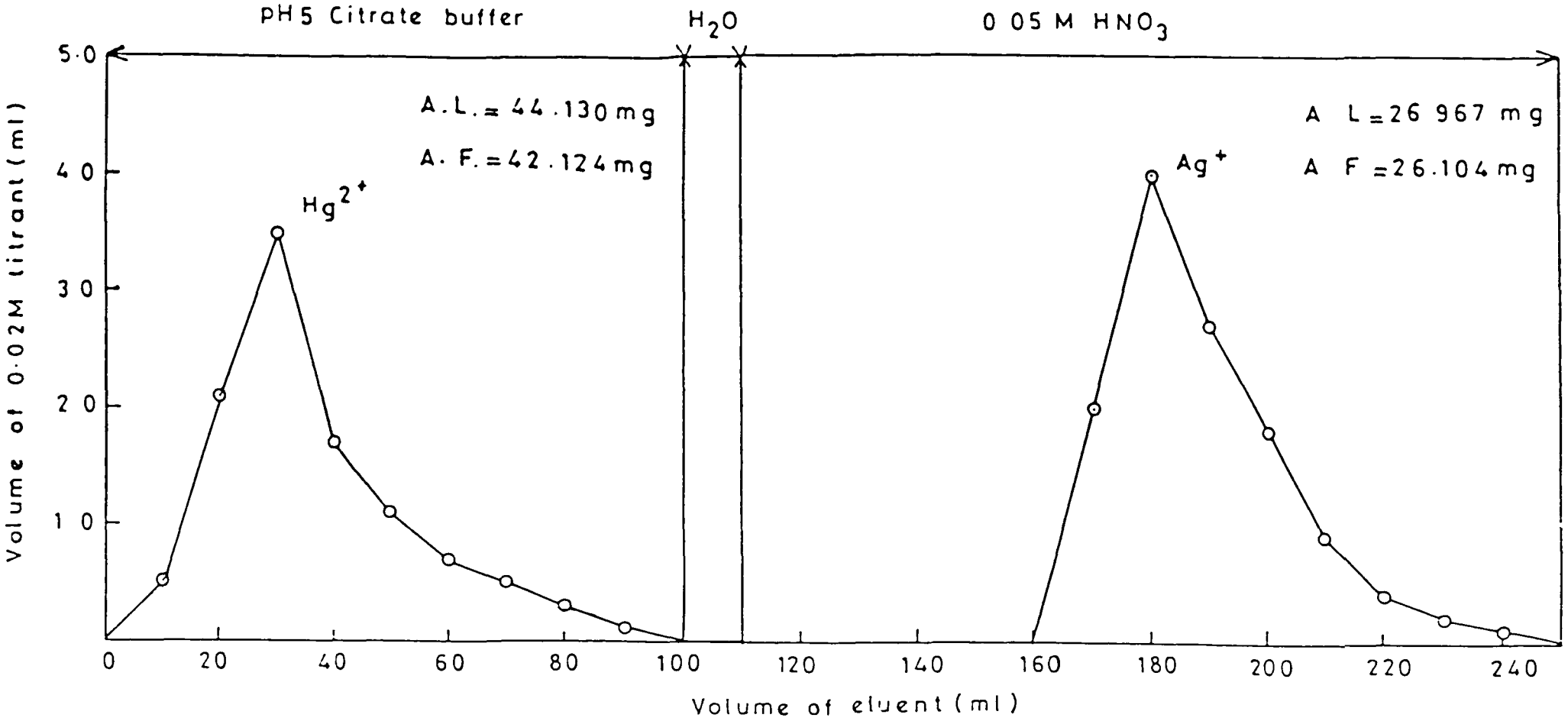

Figure II.6 Separation of Ag^+-Hg^{2+} on sodium stannosilicate column

A L =Amount loaded A F = Amount found

TABLE - II.8

Some quantitative separations on sodium stannosilicate column

Serial No.	Mixture	Eluent	Eluate (ml)	Amount loaded (mg)	Amount found (mg)	Error (%)
1	Ag^+	0.05 M HNO_3	130	26.967	25.673	4.78
	Pb^{2+}	A	110	46.620	43.926	5.77
2	Ag^+	0.05 M HNO_3	140	26.967	26.104	3.19
	Hg^{2+}	A	100	44.130	42.124	4.55
3	Ag^+	0.05 M HNO_3	130	26.967	25.888	4.00
	Cu^{2+}	B	100	15.886	14.870	6.39

A - 0.5 M sodium citrate + 0.5 M citric acid (3:2)

B - 0.02 M sodium citrate

II.3.10 Recovery of Ag^+: Uptake of Ag^+ by sodium stannosilicate was studied from silver nitrate solution of different concentrations. Sodium stannosilicate (0.5 g) was shaked with 50 ml of silver nitrate solution at 25±1°C for 6 hours. The supernatant liquid was titrated for the determination of Ag^+ left. The results are given in Table II.9.

TABLE - II.9

Uptake of Ag^+ by sodium stannosilicate from silver nitrate solution of different concentrations

Serial No.	Concentration of $AgNO_3$ solution	Volume of solution (ml)	meq of Ag^+	Uptake of Ag^+ meq/0.5 g
1	0.2 M	20	4.0	1.125
2	0.15 M	20	3.0	1.125
3	0.1 M	20	2.0	1.125
4	0.05 M	20	1.0	T.U.
5	0.02 M	20	0.4	T.U.
6	0.01 M	20	0.2	T.U.

T.U. - Total uptake of Ag^+

Uptake of Ag^+ from solutions containing sodium ion was also studied. Sodium stannosilicate (0.5 g) was added to 50 ml of 0.02 M silver nitrate solution containing equal amount of sodium nitrate and shaked for 6 hours at 25±1°C. The supernatant liquid was titrated for the determination of Ag^+ left. It was found that total uptake of Ag^+ takes place.

II.4 DISCUSSION

It is evident from Tabel II.1 that complete precipitation occurs when sodium stannate to sodium metasilicate volume ratio is kept at 1:1. The yield of sodium stannosilicate in other mixing volume ratios is very low. From the results given in table II.2 it can be inferred that sodium stannosilicate works as an extremely weak cation exchanger and releases a small amount of hydrogen ions. The metal ion capacity is sufficiently high and varies from 0.8 to 2.25 meq g^{-1}.

Table II.3 shows the stability of sodium stannosilicate in different solvents. The values in the table show that sodium stannosilicate can be used in nearly neutral media i.e. water, salt solutions, alcohols, dilute acids and alkali without any appreciable loss. The results of thermal stability (Table II.4 and Figure II.1) show that there is a slight (3.7%) weight loss at 100°C and 8.12% weight loss at 150°C; no further weight loss is observed up to 250°C. The maximum capacity for Ag^{+}, however, remains constant throughout the temperature range studied. These results suggest that only hydration water is released by heating up to 150°C and no structural changes take place.

The chemical analysis of the exchanger sodium stannosilicate shows that the apparent ratio of Sn: Si is 1:1. The results of hydrolysis given in Table II.5 and plotted in figure II.2 show that sodium stannosilicate hydrolyses appreciably. When sodium stannosilicate is in Na^+ form there is a gradual increase in pH for up to 30 minutes, thereafter, pH remains almost constant. On the other hand, when sodium stannosilicate is in H^+ form there is a very small, gradual decrease in pH for up to 15 minutes; no further change in pH is observed after 15 minutes. The results of water sorption presented in table II.6 show that water sorption of sodium stannosilicate decreases with increasing radius (crystallographic) of the counter ion.

It is quite evident from the IR-spectrum plotted in figure II.3 that the material contains water molecule and metal oxygen bond as is fully discussed below. The structure of sodium stannosilicate is a complicated one like some silicates with other metal ions. An indication of possible structure may be discussed in the light of IR-spectrum of the compound. The IR-spectrum of the material shows four bands at 3300, 1640, 990, and 700 cm^{-1} regions. In a sample of pure water a strong band is observed at 1630 cm^{-1} and two very strong

bands around 3500 cm^{-1}. In the spectrum of the exchanger the band at 3300 cm^{-1} is very strong which can be attributed to O-H stretching frequency. A medium band around 1640 cm^{-1} can be attributed to H-O-H bending band. The O-H stretching bands merge together and is shifted to lower frequency in the spectrum of the exchanger. This is due to possibility of hydrogen-bonding. In a neat sample of sodium metasilicate there is a very strong and very broad O-H stretching band around 3280 cm^{-1} region and a very strong band around 980 cm^{-1} region due to Si-O stretching frequency. In the spectrum of the exchanger the band around 990 cm^{-1} region can be attributed to Si-O stretching frequency. Since this band is much broader, it can be attributed to Si-O-Si continuous structure. In the spectrum of the exchanger the band around 700 cm^{-1} can be attributed to Sn-O-Sn bridging system.

On the basis of chemical composition and IR analysis the exchanger may be given an apparent formula

$$Na_x (SnO_2)_y (SiO_2)_y \cdot zH_2O$$

Where z is number of moles of water of hydration.

The distribution coefficient values given in table II.7 suggest the exchanger sodium stannosilicate

to be specific for Ag^+. This may provide a good method for separation of Ag^+ from other metal ions. Based on K_d values the affinity of different metal ions for the exchanger is

$$Ag^+ > Hg^{2+} > Al^{3+} > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ca^{2+} > Sr^{2+} > Mn^{2+}$$
$$Ba^{2+} \geqslant Co^{2+} > Ni^{2+} > Mg^{2+} > Fe^{3+}$$

Some quantitative separations were achieved on a column of sodium stannosilicate (Table II.8). The order and the eluents are presented in figures II.4, II.5 and II.6. These results suggest sodium stannosilicate a useful means of separating Ag^+ from Cu^{2+}, Pb^{2+} and Hg^{2+} and other fields where the removal and recovery of Ag^+ is important.

The results given in table II.9 show that from very dilute solutions, total uptake of Ag^+ is resulted provided that total Ag^+ content of the solution is less than the maximum capacity of sodium stannosilicate. The results of uptake of Ag^+ from solutions containing sodium ion show that the selectivity for Ag^+ is so high that uptake of Ag^+ is not affected by the presence of sodium. This shows the importance of sodium stannosilicate in the recovery of precious metals.

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Chapter III

Ion Exchange Equilibria of Alkaline Earth Metal Ions with Sodium Ion on Sodium Stannosilicate

III.1 INTRODUCTION

Equilibrium studies on ion exchangers are being made with great interest. Several theories for ion exchange equilibria have been developed and tried on a number of ion exchangers. Equilibria on synthetic organic resins have been studied by several authors[1,2]. The thermodynamics of ion exchange on inorganic ion exchangers is considerably simplified as compared with the organic ion exchange resins, due to their rigid structure, little swelling and relatively small changes in water content between different cationic forms of the inorganic ion exchangers. The first study of ion exchange equilibria on zirconium phosphate deals with the Li^+-H^+, Na^+-H^+ and K^+-H^+ exchange.[3] Abe, Amphlett, Nancollas, Costantino and Toracca performed some admirable studies of ion exchange on zirconium phosphate for alkali metal ions[4-10]. Larsen and Cilley made these studies on cerium phosphate[11]. Ion exchange isotherms for Li^+-K^+ exchange were studied by Alberti and Costantino on crystalline zirconium phosphate[12]. Baetsle[13] reported the ion exchange equilibria for Rb^+, Cs^+, Sr^{2+}, Ca^{2+}, Ce^{3+} and Eu^{3+} with hydrogen ion on zirconium phosphate both at micro and macro concentration levels in the temperature range 5-71°C. Ion exchange

equilibria for alkali metal ions on zirconium phosphate have also been studied by Ruvarac[14]. The thermodynamics of ion exchange for alkali and alkaline earth metal ions on ferric antimonate[15,16] and niobium arsenate[17] have been made in our laboratories. Abe and Furuki studied exchange equilibria of alkali metal ions with hydrogen ion on tin antimonate[18]. They also reported the hypothetical thermodynamic data on "zero loading" on the ion exchange reaction. Thermodynamic treatment of exchange of alkali metal ions with hydrogen ion on $\alpha$and γ titanium phosphate have also been studied[19-21]. The thermodynamics of ion exchange on zeolites have been extensively studied by Barrer[22-25], Dyer[26] and Frysinger[27]. They studied the effect of temperature on ion exchange equilibria with different zeolites in various cationic forms. Several analogues of the zeolites have been synthesized and studied by many workers[28,29].

The present report describes the influence of temperature on the equilibria of Mg^{2+}-Na^{+}, Ca^{2+}-Na^{+}, Sr^{2+}-Na^{+} and Ba^{2+}-Na^{+} exchange on an analogue of the zeolites, sodium stannosilicate, at a constant ionic strength within the temperature range from 30-60°C. A simple approach has been applied and various thermodynamic parameters are calculated. Hypothetical thermodynamic data in infinitesimal concentration are also reported.

III.2 EXPERIMENTAL

III.2.1 Reagents: Stannic chloride pentahydrate (Reachim) and sodium metasilicate (Loba) were used. All other chemicals used were of A.R. grade.

III.2.2 Apparatus: An electric temperature controlled SICO shaker and pH-meter model Li-10 (India) were used for shaking and pH measurements respectively.

III.2.3 Preparation of Sodium Stannate Solution: For this purpose 0.5 molar sodium hydroxide solution was added to 0.1 molar stannic chloride solution and pH was adjusted to 10. The solution initially turbid, turned into a clear solution of sodium stannate on heating at 60±1°C.

III.2.4 Synthesis of Sodium Stannosilicate: Sodium stannosilicate was synthesized by mixing 0.1 molar sodium metasilicate solution with 0.1 molar sodium stannate solution in a volume ratio 1:1. This mixture was refluxed for 24 hours and the resulting white precipitate was allowed to settle overnight. It was then filtered and dried at 60±1°C in an air oven. The dried product was broken into small granules by simply immersing in

distilled water. These granules were washed several times with distilled water and dried at 60±1°C. To convert the exchanger in Na^+ form it was kept in 1.0 molar sodium nitrate solution overnight.

III.2.5 Equilibrium Studies: The equilibrium experiments were performed using batch technique. The solution (20 ml) containing sodium nitrate and appropriate alkaline earth metal nitrate having constant ionic strength 0.10 was taken in a stoppered conical flask. To this flask 0.2 g exchanger in sodium form was added and shaked in a temperature controlled shaker for 6 hours at the required temperature. The supernatant solution was then titrated with 0.02 molar EDTA solution for the determination of the cations left.

Reversibility experiments were performed by equiliberating 0.2 g exchanger in a particular metal ion form with that metal ion and sodium nitrate solution having a constant ionic strength at the required equiliberating temperature and titrating the supernatant liquid with 0.02 molar EDTA for the determination of cations left.

III.3 RESULTS

The ion exchange isotherms for various cations at different temperatures are plotted in Figures III.1-III.4 and the results of equivalent fractions of metal ions, selectivity coefficients and thermodynamic equilibrium constants are given in Tables III.1-III.4.

TABLE III.1

Equivalent fractions of Mg^{2+}, selectivity coefficients and thermodynamic equilibrium constants for Mg^{2+}-Na^{+} exchange on sodium stannosilicate

Serial No.	$\bar{X}_{Mg}$	X_{Mg}	K_c	K_a
	(a) Mg^{2+}-Na^{+} at 30±1°C			
1	0.3000	0.0245	31.9377	
2	0.4000	0.0690	18.7455	
3	0.4500	0.1216	12.6770	
4	0.5000	0.1872	9.4794	
5	0.5500	0.2513	8.1368	0.29×10^2
6	0.6500	0.3189	10.3666	
7	0.6500	0.4128	5.9525	
8	0.7000	0.5125	4.8439	
9	0.7500	0.6284	3.5415	
10	0.8000	0.7647	1.9448	

Contd...

Serial No.	$\bar{X}_{Mg}$	X_{Mg}	K_c	K_a
	(b) Mg^{2+}-Na^+ at 45±1°C			
1	0.4000	0.0163	88.5902	
2	0.5000	0.0613	38.6112	
3	0.5500	0.1126	25.5111	
4	0.6000	0.1791	18.9499	
5	0.6500	0.2374	17.4574	1.06×10^2
6	0.7000	0.3118	15.8672	
7	0.7500	0.3965	14.8041	
8	0.8000	0.4958	13.7727	
9	0.8000	0.6174	6.3686	
10	0.8500	0.7582	3.9125	
	(c) Mg^{2+}-Na^+ at 60±1°C			
1	0.4750	0.0121	186.6835	
2	0.6000	0.0549	81.9416	
3	0.6250	0.1111	42.4521	
4	0.6750	0.1710	34.4937	
5	0.7250	0.2376	31.4979	2.32×10^2
6	0.7500	0.3158	23.8905	
7	0.7750	0.4045	18.0249	
8	0.8000	0.5060	12.9546	
9	0.8375	0.6207	9.8126	
10	0.8500	0.7606	3.8231	

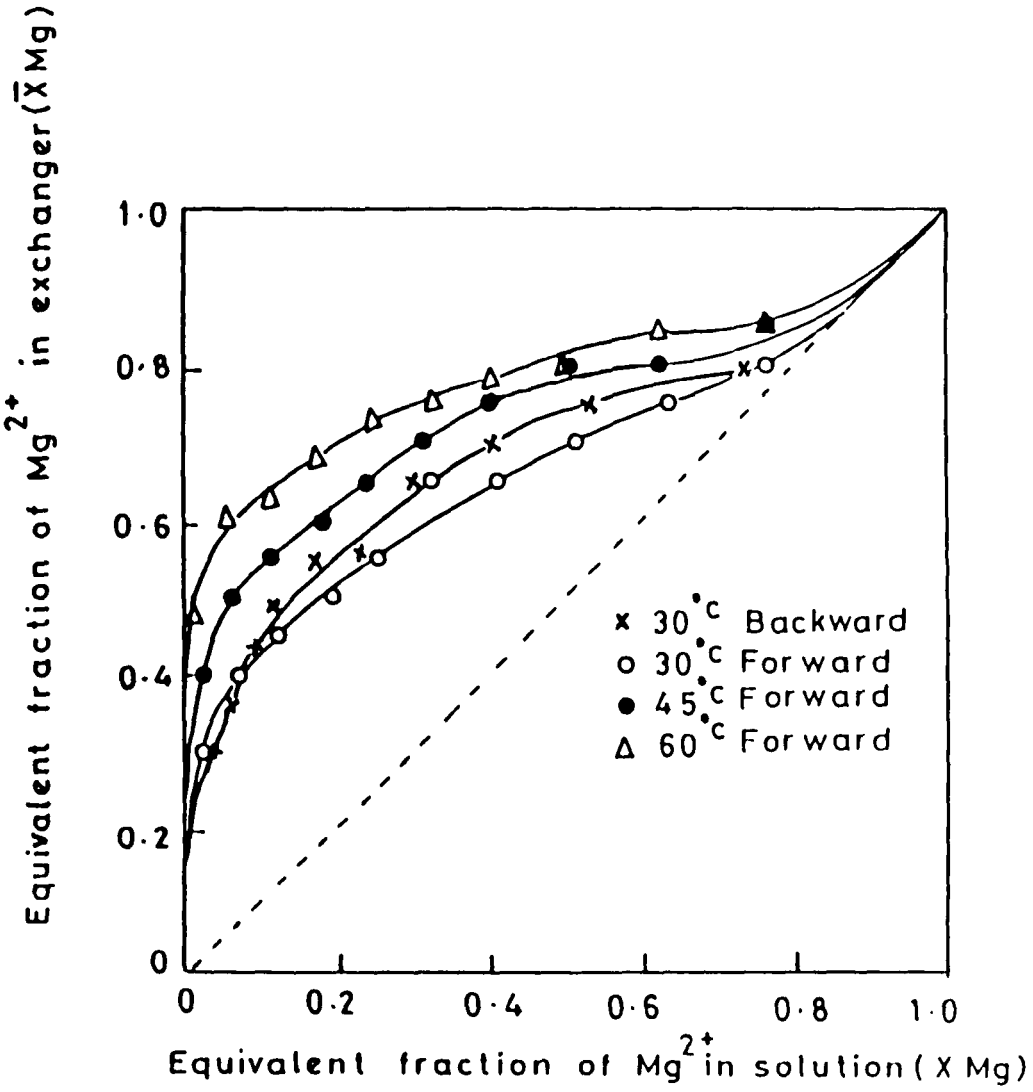

Figure III.1 Ion exchange isotherm of Mg^{2+}-Na^{+} exchange on sodium stannosilicate

TABLE - III.2

Equivalent fractions of Ca^{2+}, selectivity coefficients and thermodynamic equilibrium constants for Ca^{2+}-Na^{+} exchange on sodium stannosilicate

Serial No.	$\bar{X}_{Ca}$	X_{Ca}	K_c	K_a
	(a) Ca^{2+}-Na^{+} at 30±1°C			
1	0.3778	0.0143	101.7956	
2	0.4444	0.0598	32.6710	
3	0.5111	0.1101	23.6121	
4	0.5333	0.1714	15.0574	
5	0.5556	0.2405	10.3592	0.51×10^2
6	0.5778	0.3189	7.2391	
7	0.6000	0.4087	4.9251	
8	0.6667	0.5031	4.5128	
9	0.6667	0.6284	2.0246	
10	0.7556	0.7518	1.5913	

Contd...

Serial No.	$\bar{X}_{Ca}$	X_{Ca}	K_c	K_a
	(b) Ca^{2+}-Na^{+} at 45±1°C			
1	0.4333	0.0091	223.4982	
2	0.5556	0.0486	80.4410	
3	0.5778	0.1027	39.0139	
4	0.6000	0.1631	24.7228	
5	0.6333	0.2296	18.6905	1.47×10^2
6	0.6667	0.3048	13.8530	
7	0.6667	0.4083	7.9005	
8	0.6889	0.4985	5.5132	
9	0.7111	0.6174	3.1012	
10	0.7778	0.7454	2.1032	
	(b) Ca^{2+}-Na^{+} at 60±1°C			
1	0.4550	0.0081	285.6556	
2	0.5778	0.0480	93.9609	
3	0.6111	0.1020	49.0414	
4	0.6667	0.1589	41.0209	
5	0.7000	0.2252	31.8302	3.14×10^2
6	0.7333	0.3000	25.8514	
7	0.7667	0.3848	21.2700	
8	0.8000	0.4819	17.1031	
9	0.8111	0.5993	9.3493	
10	0.8222	0.7314	3.9386	

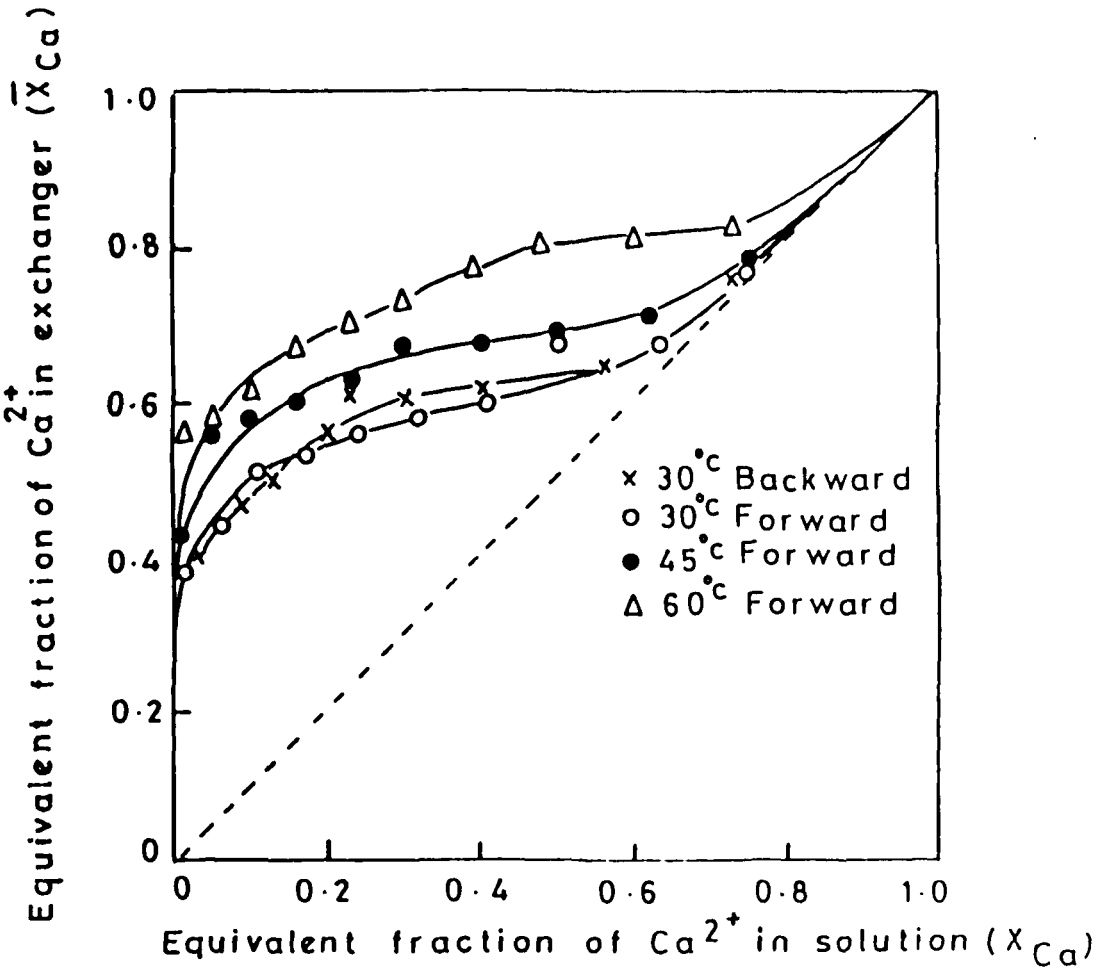

Figure III.2 Ion exchange isotherm of Ca^{2+}-Na^{+} exchange on sodium stannosilicate

TABLE - III.3

Equivalent fractions of Sr^{2+}, selectivity coefficients and thermodynamic equilibrium constants for Sr^{2+}-Na^{+} exchange on sodium stannosilicate

Serial No.	$\bar{X}_{Sr}$	X_{Sr}	K_c	K_a
	(a) Sr^{2+}-Na^{+} at 30±1°C			
1	0.4111	0.0122	157.7212	
2	0.4889	0.0573	48.2890	
3	0.5222	0.1119	26.8217	
4	0.5556	0.2269	12.3282	
5	0.5889	0.2406	13.8944	0.96×10^2
6	0.6444	0.3138	12.7212	
7	0.6556	0.4046	8.0566	
8	0.7111	0.5000	7.0869	
9	0.7444	0.6151	4.5655	
10	0.7778	0.7500	2.1840	

Contd...

Serial No.	$\bar{X}_{Sr}$	X_{Sr}	K_c	K_a
	(b) Sr^{2+}-Na^+ at 45±1°C			
1	0.4222	0.0111	185.3499	
2	0.5333	0.0529	69.0686	
3	0.5444	0.1094	31.6335	
4	0.6222	0.1643	30.8261	
5	0.6556	0.2316	23.4422	1.59×10^2
6	0.6889	0.3069	18.5353	
7	0.7222	0.3927	14.6214	
8	0.7222	0.4977	7.8922	
9	0.8111	0.5993	10.1298	
10	0.8111	0.7407	3.4326	
	(c) Sr^{2+}-Na^+ at 60±1°C			
1	0.4444	0.0090	261.3384	
2	0.5778	0.0484	100.8913	
3	0.6667	0.0959	85.0987	
4	0.6889	0.1562	53.7763	
5	0.7222	0.2222	42.3871	3.51×10^2
6	0.7444	0.2983	31.2884	
7	0.7556	0.3868	20.4577	
8	0.8000	0.4819	18.5331	
9	0.8222	0.5967	11.7941	
10	0.8333	0.7345	4.8056	

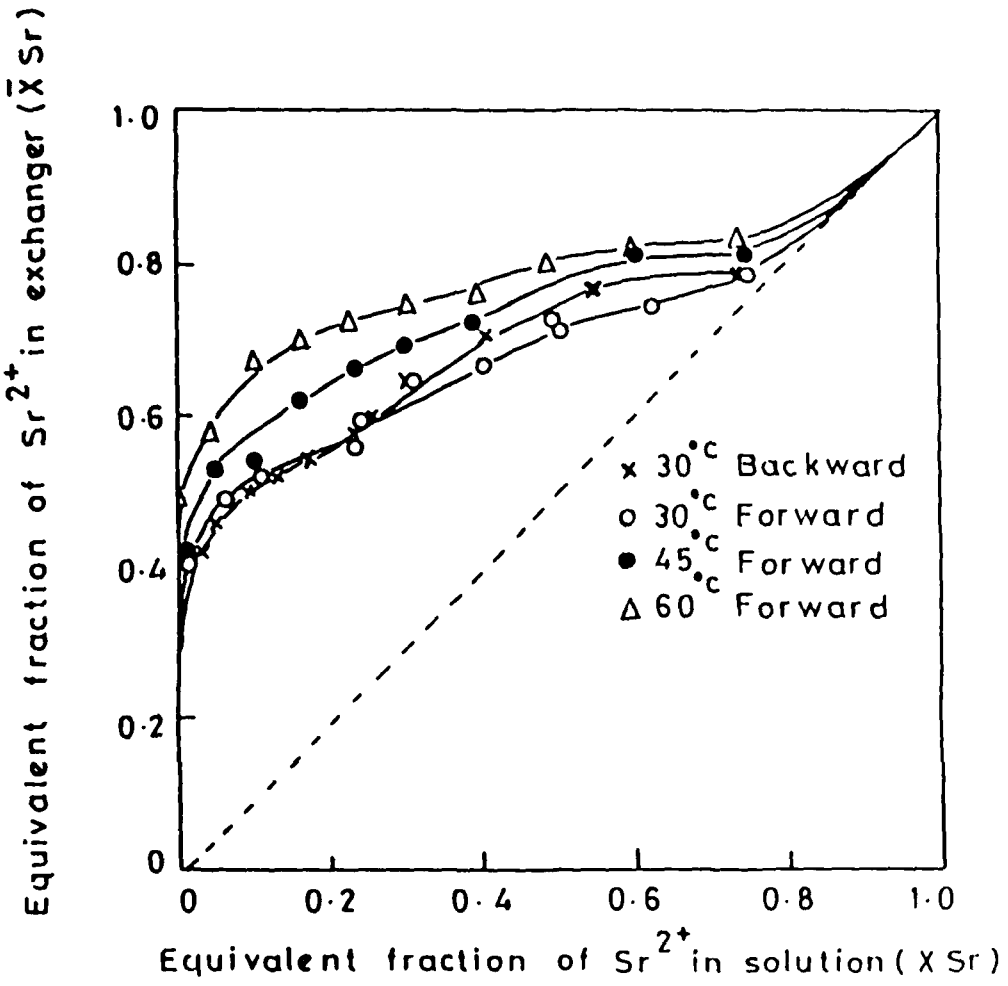

Figure III.3 Ion exchange isotherm of Sr^{2+}-Na^{+} exchange on sodium stannosilicate

TABLE - III.4

Equivalent fractions of Ba^{2+}, selectivity coefficients and thermodynamic equilibrium constants for Ba^{2+}-Na^{+} exchange on sodium stannosilicate

Serial No.	$\bar{X}_{Ba}$	X_{Ba}	K_c	K_a
	(a) Ba^{2+}-Na^{+} at 30±1°C			
1	0.4500	0.0056	436.9887	
2	0.5333	0.0487	75.6922	
3	0.5556	0.1021	36.9567	
4	0.6000	0.1591	27.7267	
5	0.6111	0.2278	17.5951	3.76×10^2
6	0.6222	0.3062	11.4004	
7	0.6778	0.3884	10.4606	
8	0.7111	0.4875	7.6366	
9	0.7444	0.6034	4.9412	
10	0.7778	0.7407	2.3790	

Contd...

Serial No.	$\bar{X}_{Ba}$	X_{Ba}	K_c	K_a
	(b) Ba^{2+}-Na^{+} at 45±1°C			
1	0.4777	0.0041	704.7120	
2	0.5556	0.0466	91.2909	
3	0.5889	0.0984	47.8882	
4	0.6222	0.1564	33.0070	
5	0.6556	0.2217	25.1241	9.45×10^2
6	0.6889	0.2957	19.8641	
7	0.7444	0.3764	19.5838	
8	0.8000	0.4691	19.9912	
9	0.8500	0.5611	21.5763	
10	0.8889	0.7091	14.2973	
	(c) Ba^{2+}-Na^{+} at 60±1°C			
1	0.5000	0.0020	1656.9523	
2	0.6111	0.0431	142.8043	
3	0.6333	0.0935	68.8590	
4	0.6556	0.1512	43.3856	
5	0.7111	0.2140	40.9181	1.97×10^3
6	0.7333	0.2889	30.0191	
7	0.8000	0.3667	36.3904	
8	0.8444	0.4601	35.9456	
9	0.9000	0.5662	49.7623	
10	0.9444	0.6937	68.7349	

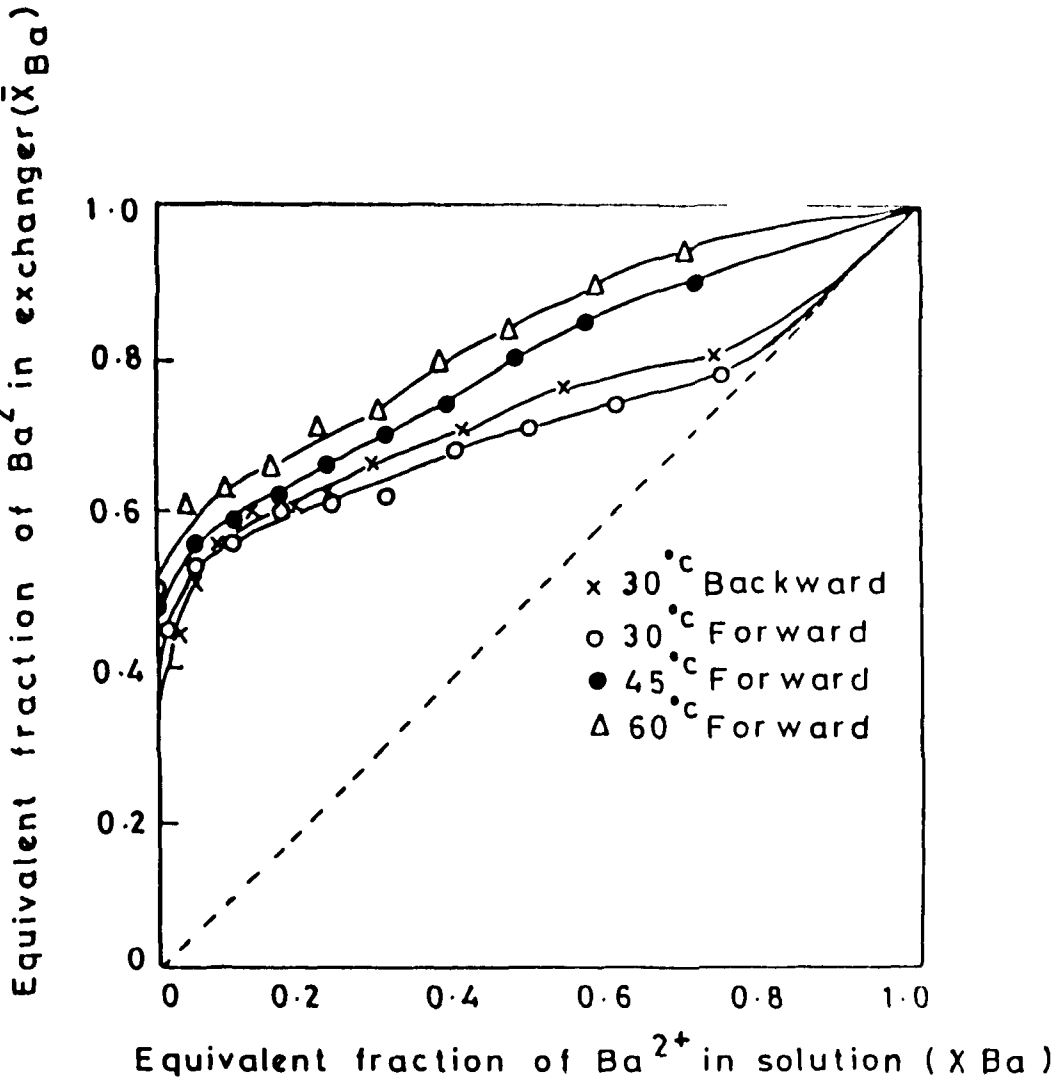

Figure III.4 Ion exchange isotherm of Ba^{2+}-Na^{+} exchange on sodium stannosilicate

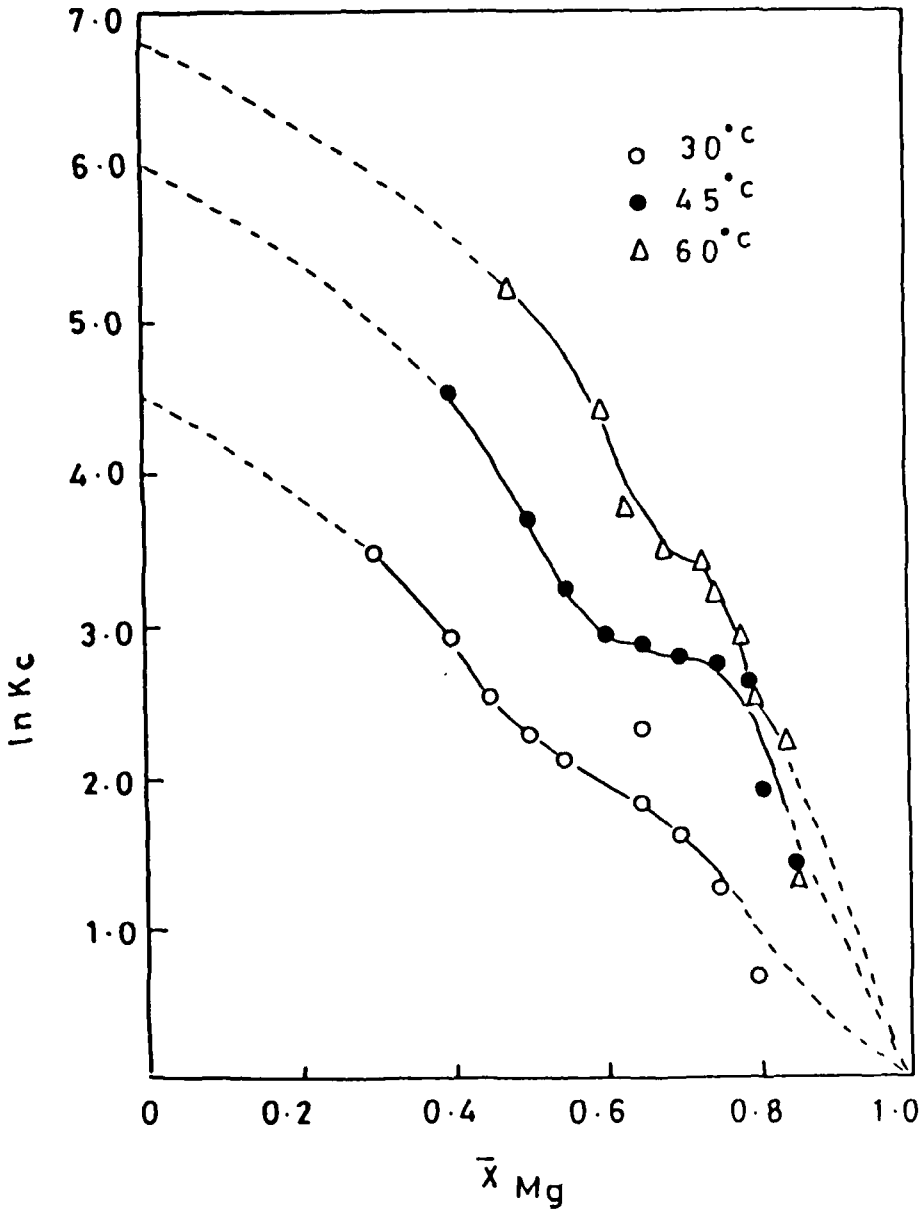

Figure III.5 ln of selectivity coefficient versus equivalent fraction of Mg^{2+} in exchanger phase

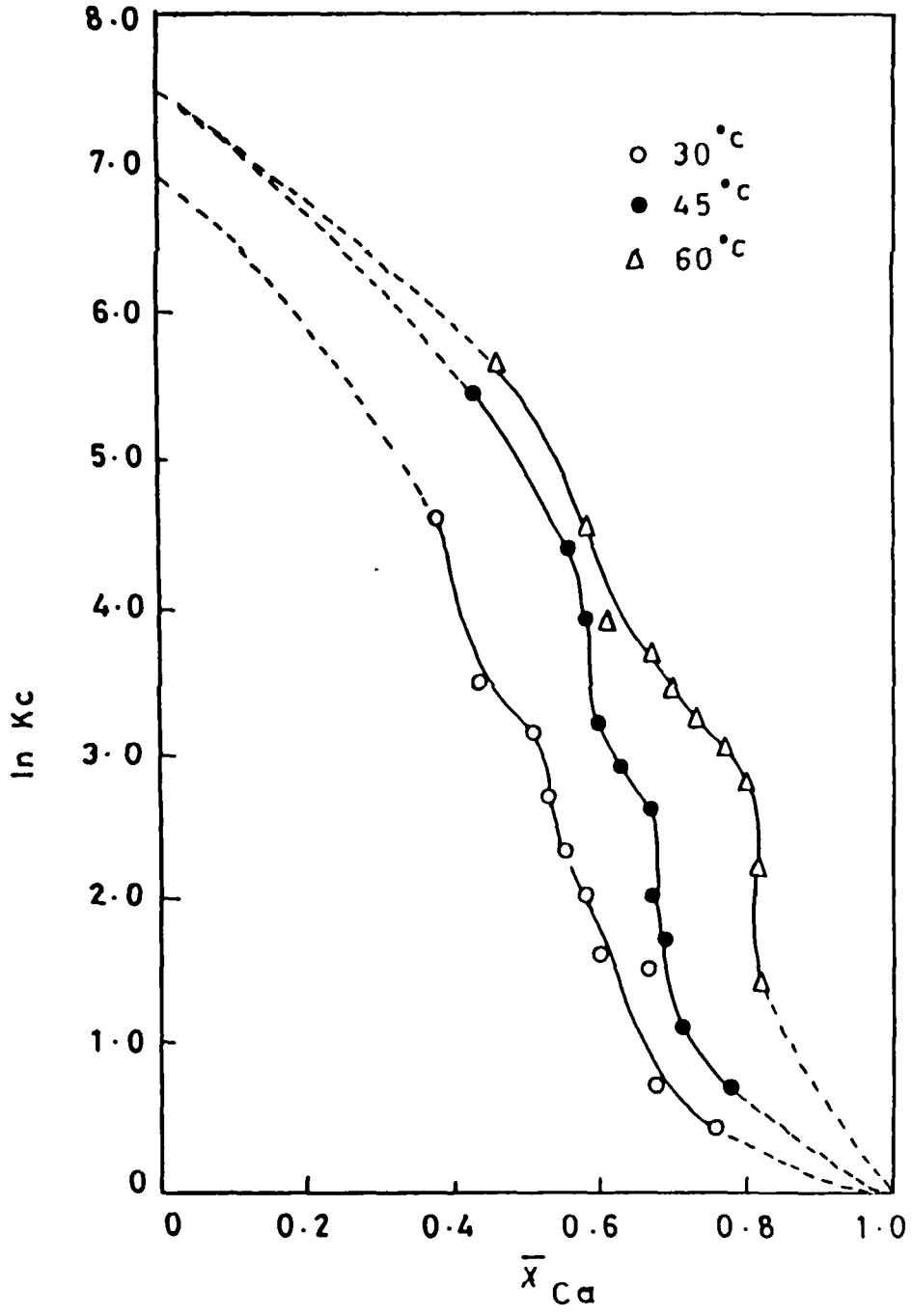

Figure III.6 ln of selectivity coefficient versus equivalent fraction of Ca^{2+} in exchanger phase

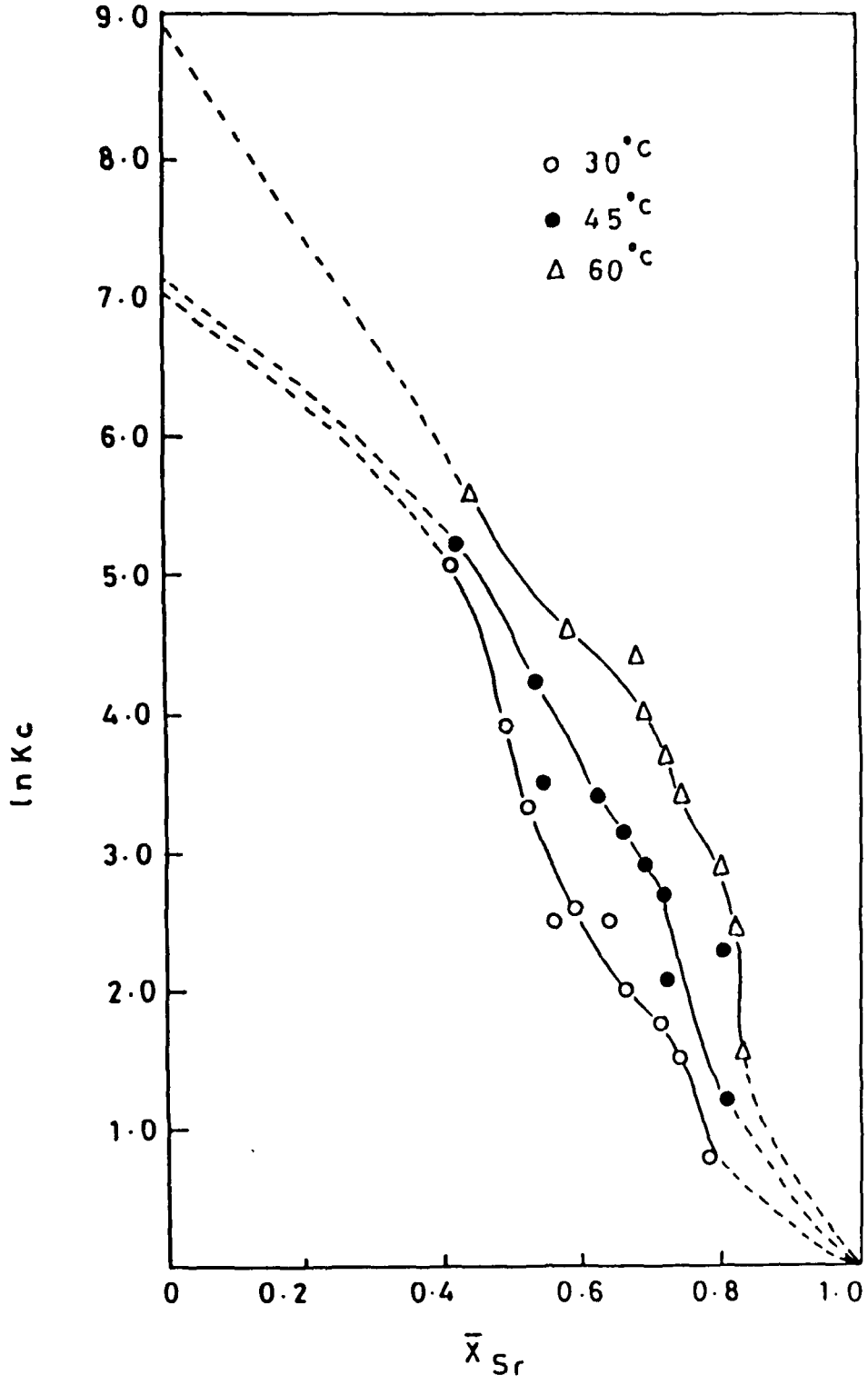

Figure III.7 ln of selectivity coefficient versus equivalent fraction of Sr^{2+} in exchanger phase

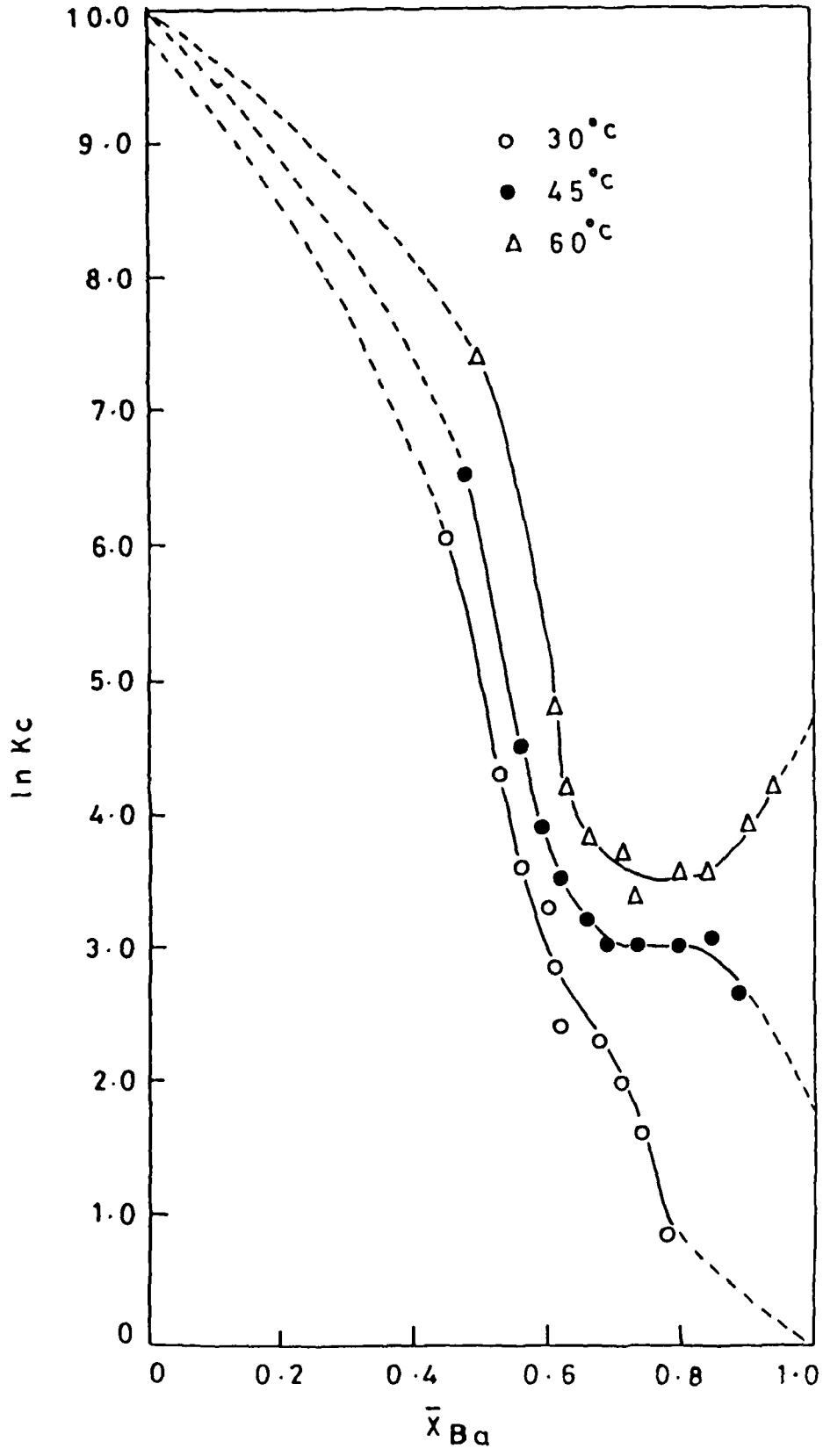

Figure III.8 ln of selectivity coefficient versus equivalent fraction of Ba^{2+} in exchanger phase

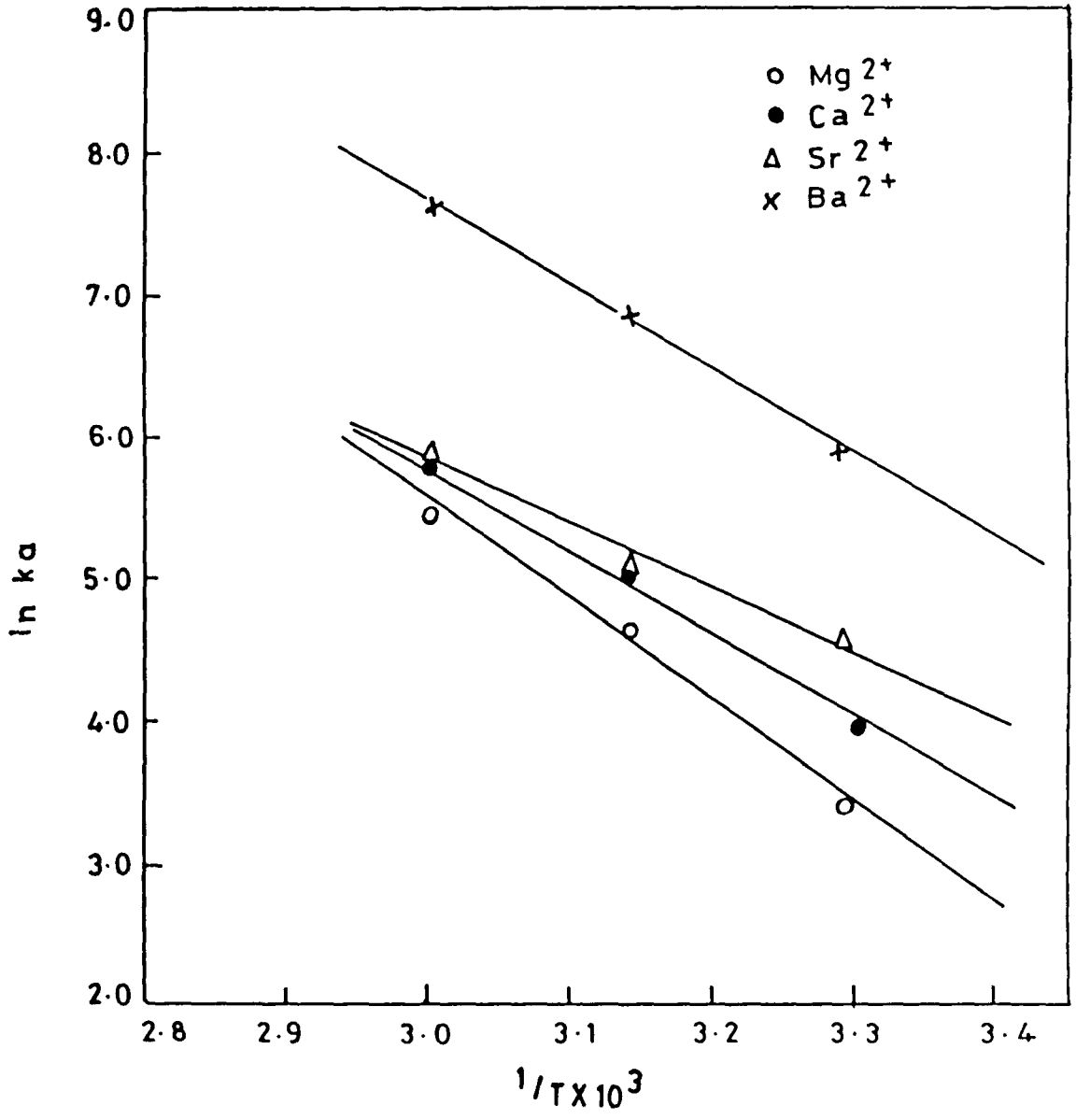

Figure III.9 Plots of ln K_a versus 1/T for alkaline earth metal ions

The plots of ln K_c versus equivalent fractions of cations in exchanger phase are presented in Figures III.5-III.8. The thermodynamic equilibrium constants calculated from these plots are given in Tables III.1-III.4.

The values of enthalpy change $\Delta H°$ were obtained from the plots of ln K_a versus 1/T presented in Figure III.9 and free energy change $\Delta G°$ and entropy change $\Delta S°$ were calculated using appropriate equations. The values of various thermodynamic parameters are given in Tables III.5-III.8. Hypothetical thermodynamic data at "zero loading" on ion exchange reaction at 30°C are given in Table III.9.

TABLE - III.5

Thermodynamic parameters for Mg^{2+}-Na^{+} exchange on sodium stannosilicate at constant ionic strength

Thermodynamic Parameter	30±1°C	45±1°C	60±1°C
K_a	0.29×10^2	1.06×10^2	2.32×10^2
$\Delta G°$ (KJ/mole)	-4.23	-6.17	-7.54
$\Delta H°$ (KJ/mole)	58.20		
$\Delta S°$ (J/mole/degree)	205.94	202.33	197.33

TABLE - III.6

Thermodynamic parameters for Ca^{2+}-Na^{+} exchange on sodium stannosilicate at constant ionic strength

Thermodynamic Parameter	30±1°C	45±1°C	60±1°C
K_a	0.51×10^2	1.47×10^2	3.14×10^2
$\Delta G°$ (KJ/mole)	-4.95	-6.60	-7.96
$\Delta H°$ (KJ/mole)	47.10		
$\Delta S°$ (J/mole/degree)	171.70	168.79	165.27

TABLE - III.7

Thermodynamic parameters for Sr^{2+}-Na^{+} exchange on sodium stannosilicate at constant ionic strength

Thermodynamic Parameter	30±1°C	45±1°C	60±1°C
K_a	0.96×10^2	1.59×10^2	3.51×10^2
$\Delta G°$ (KJ/mole)	-5.75	-6.71	-8.12
$\Delta H°$ (KJ/mole)	37.40		
$\Delta S°$ (J/mole/degree)	142.34	138.65	136.64

TABLE - III.8

Thermodynamic parameters for Ba^{2+}-Na^{+} exchange on sodium stannosilicate at constant ionic strength

Thermodynamic Parameter	30±1°C	45±1°C	60±1°C
K_a	3.76×10^2	9.45×10^2	1.97×10^3
$\Delta G°$ (KJ/mole)	-7.47	-9.06	-10.50
$\Delta H°$ (KJ/mole)	47.80		
$\Delta S°$ (J/mole/degree)	182.32	178.72	175.00

TABLE - III.9

Hypothetical thermodynamic data on "zero loading" on the ion exchange reaction at 30±1°C.

Hypothetical thermodynamic data	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$(\ln K_c)_{\bar{X}_M \to 0}$	4.50	6.90	7.00	9.75
$(\Delta G°)_{\bar{X}_M \to 0}$ (KJ/mole)	-5.67	-8.70	-8.82	-12.29
$(\Delta H°)_{\bar{X}_M \to 0}$ (KJ/mole)	0.00	0.00	0.00	0.00
$(\Delta S°)_{\bar{X}_M \to 0}$ (J/mole/degree)	18.70	28.70	29.09	40.54

III.4 DISCUSSION

Sodium stannosilicate in sodium form behaves as a weak cation exchanger. Figures III.1-III.4 show the reversibility of exchange of metal ions with sodium form of sodium stannosilicate. The ion exchange reaction with bivalent metal ions on sodium stannosilicate may be written as

$$2\ \bar{Na}^{+} + M^{2+} \rightleftharpoons \bar{M}^{2+} + 2\ Na^{+} \quad \ldots\ (1)$$

Where the barred quantities refer to the exchanger phase and the unbarred to the solution phase.

Ion exchange process being stoichiometric will liberate an amount of sodium ion equivalent to the metal ion taken by the exchanger. Such an exchange is plotted in figures III.1-III.4 in the form of ion exchange isotherms for the forward and backward processes. An examination of these exchange isotherms shows that for exchange carried out at constant ionic strength all exchange isotherms are above the diagonal indicating that alkaline earth metal ions are preferred to sodium by sodium stannosilicate. The curves are S shaped for Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions with different selectivities. Sigmoid curves as those in figures III.1-III.4

have been observed in a number of ion exchange isotherm studies particularly with zeolites[24]. The affinity for alkaline earth metal ions increases at higher temperatures. The isotherms indicate that uptake of barium ion occurs to a greater extent than those of other alkaline earth metal ions. The preference of alkaline earth metal ions is in the order of

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$$

The selectivity coefficient values for alkaline earth metal ion exchange with sodium form of sodium stannosilicate (equation 1) are calculated from the relationship[30]

$$K_c = \frac{\bar{X}_M \cdot X_{Na}^2}{\bar{X}_{Na}^2 \cdot X_M} \cdot \frac{\gamma_{Na}^2}{\gamma_M} \qquad \ldots\ldots(2)$$

Where $\bar{X}_M$ and $\bar{X}_{Na}$ are the equivalent fractions of metal and sodium ion respectively in the exchanger phase, X_M and X_{Na} the equivalent fractions of metal and sodium ion respectively in solution phase, γ_{Na} and γ_M the activity coefficients of sodium and metal ions respectively in the solution phase. The activity coefficients of the cations in the solution phase are calculated using Debye-Huckel equation -

$$- \log \gamma_i = \frac{A.Z_i^2 \sqrt{u}}{1 + B.a_i\sqrt{u}} \qquad \ldots\ldots(3)$$

Where A and B are constants, a_i the ion size parameter, u the ionic strength and Z_i the charge on the ion i. The values of A,B and a_i are taken from that given by Freiser and Fernando[31].

The values of selectivity coefficients are given in Tables III.1-III.4 and plotted in figures III.5-III.8. These results indicate that the value of K_c does not remain constant but varies with the equivalent fraction of alkaline earth metal ion, $\bar{X}_M$ in the exchanger phase and hence the thermodynamic equilibrium constant can be evaluated. The thermodynamic equilibrium constant, K_a is calculated from the expression given by Gains and Thomas[32] for the exchange involving cations A and B with charges Z_A and Z_B respectively.

$$\ln K_a = Z_A - Z_B + \int_0^1 \ln K_c . d\bar{X}_M \qquad \ldots\ldots(4)$$

The magnitude of the charges on A and B are known, therefore the first term in equation 4 is readily calculated. The second term is obtained by integrating below the curve of $\ln K_c$ as a function of $\bar{X}_M$ (figures III.5-III.8). The values of K_a are presented in

tables III.1-III.4. These results show that alkaline earth metal ions are preferred to sodium ion by the sodium form of the exchanger at all temperatures from 30-60°C. However, the degree of selectivity increases at higher temperatures. The selectivity order of alkaline earth metal ions remains the same ie. $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

The standard free energy change $\Delta G°$ for the exchange process is calculated from the thermodynamic equilibrium constant using equation

$$\Delta G° = - \frac{R.T}{Z_{Na} \cdot Z_M} . \ln K_a \qquad ....(5)$$

Where R is universal gas constant, T the absolute temperature and Z_{Na}, Z_M the valencies of competing ionic speices. The results of standard free energy change presented in tables III.5-III.8 indicate that free energy change is negative over all the temperatures during the exchange of alkaline earth metal ion on sodium form of the sodium stannosilicate. This shows that at all temperatures the exchange process has a natural tendency to move spontaneously.

The standard enthalpy change has been calculated using Van't Hoff equation -

$$\Delta H^\circ = - R \frac{d \ln K_a}{d\ 1/T} \qquad \ldots.(6)$$

Standard enthalpy change is evaluated from the plots of ln K_a against 1/T (figure III.9). The results are presented in tables III.5-III.8. These results show that standard enthalpy change is positive. This indicates that the reaction is endothermic and a rise in temperature favours the reaction. It means binding energy of one atom of alkaline earth metal is higher than that of one atom of sodium.

The standard entropy change is calcuated from ΔH° and ΔG° values using the equation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad \ldots.(7)$$

The results of standard entropy change (Tables III.5-III.8) show a gain in entropy. This indicates lesser order produced in the forward reaction during alkaline earth metal transfer to sodium stannosilicate. Ingoing of ions from solution to the exchanger phase results in a less ordered structure to the alkaline earth metal ions in the matrix which results in the mobilization and an increase in the degree of freedom of alkaline earth metal ions in the exchanger phase. This contributes to an increase in entropy. The passage of sodium ion

from exchanger to the solution phase results in lesser ordering of water and a further increase in entropy.

Hypothetical thermodynamic data in infinitesimal concentration are calculated for interpretation of the selectivity of the alkaline earth metal ions in the trace amounts of sodium stannosilicate. The values of $(\ln K_c)_{\bar{X}_M} \longrightarrow 0$ are obtained by extrapolating to zero loading[33] of alkaline earth metal ions in figures III.5-III.8. From these values the hypothetical thermodynamic data are calculated by the similar treatment as for the overall equilibrium constant. The accuracy of these values may be higher than those of the latter. Hypothetical thermodynamic data on "zero loading" on the ion exchange reaction at 30°C are given in Table III.9. The calculated $(\Delta H°)_{\bar{X}_M} \longrightarrow 0$ values indicate that there is no enthalpy change in the reaction when alkaline earth metal ion concentration in the exchanger phase approaches to zero over the entire temperature range while the $(\Delta S°)_{\bar{X}_M} \longrightarrow 0$ increases with increasing ionic radii of the alkaline earth metal ions.

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Chapter IV

Sorption Equilibria of Lead (II) on Some Indian Soils : The Natural Ion Exchangers

IV.1 INTRODUCTION

Environmental pollution is increasing day by day due to increase in industrialization and urbanization. The land disposal of municipal and industrial sludges has received a considerable attention in recent years. The content of lead and other heavy metals in sludges can be high[1] and hence there is a potential hazard of contaminating soils and plants with excess amount of these metals. There is an abundance of information dealing with the uptake of lead by plants and soils[2,3]. This is considered to have negative effect on the quality of food and fodder[4]. Lead is retained in soils by ion exchange/adsorption and its accumulation in soils may cause clinical problems in animals and human beings. Considerable work has been done on the adsorption behaviour of lead (II) on montmorillonite, Kaolinite and Illite[5]. Harter[6] has studied the adsorption of lead and copper by some soils of Northern United States.

In the present paper sorption equilibria of lead (II) on two different types of Indian soils have been studied at 30 and 50°C. Various properties such as cation exchange capacity, pH, electrical conductance and percentage of organic matter present in the two soils

have been studied. The sorption data are analysed in terms of sorption isotherms, distribution coefficient, Langmuir equation and various thermodynamic parameters. The purpose of this study was to understand the basic chemistry of lead(II) in soils and to predict the nature of interaction of this heavy metal with the soils.

IV.2 EXPERIMENTAL

IV.2.1 Reagents: Lead(II) nitrate [$Pb(NO_3)_2$] from Loba Chemie, India was used. All other chemicals used were of Anal. R. grade.

IV.2.2 Apparatus: An electric temperature controlled SICO shaker was used for shaking; an Elico pH meter model Li-10 for pH measurements; a systronic conductivity meter dip type cell for electrical conductance measurement and GBC 902 Double-beam Atomic Absorption Spectrophotometer for the determination of Lead(II).

IV.2.3 Preparation of Soil Samples: The soils used in the present investigation were surface samples (depth 0-30 cm) obtained from Aligarh district (U.P.) and Haldighati (Rajasthan). Both the soils were ground in a hammer mill fitted with a 100 mesh size sieve to obtain samples with a small and nearly homogeneous particle size.

IV.2.4 Cation Exchange Capacity (C.E.C.): The ion exchange capacity for H^+ ion was determined by Ganguli's method[7]. The soil sample (1g) in H^+ form was kept with 20 ml saturated solution of KCl at 25±1°C overnight and the H^+ ions liberated were titrated with 0.1 M NaOH solution

till the pink colour persisted for about three minutes. The exchangeable calcium ion was determined by sodium acetate method as given by Jackson[8]. The capacity for lead(II) ion was determined by shaking the soil sample (1g) with 25 ml 0.01 M aqueous lead(II) nitrate solution at 25±1°C and determining the lead(II) ions left in the supernatent liquid by atomic absorption spectrometry at 283.3 nm.

IV.2.5 pH and Electrical Conductance: For this purpose a 1:5 soil water suspension was prepared by adding 10g soil sample to 50 ml distilled water in a stoppered conical flask. The suspension was kept overnight and pH of the supernatant liquid was measured at 25±1°C. The electrical conductance (E.C.) of the soil water suspension was measured with a systronic conductivity meter dip type cell[8].

IV.2.6 Percentage of Organic Matter: The organic matter (O.M.) content of the soil was determined by the method proposed by walkley and Black[9]. For this purpose, 2g soil sample was taken in a 500 ml conical flask. To this flask, 10 ml of 1.0 N potassium dichromate and 20 ml of concentrated sulfuric acid were added. The flask was shaked vigorously and allowed to cool for 30 minutes.

Thereafter, 200 ml of distilled water, 10 ml of phosphoric acid and 1 ml of diphenylamine indicator were added to it. The amount of unreacted potassium dichromate was titrated with 0.5 N ferrous ammonium sulfate solution till the violet colour changes to purple and finally to green. Reagent blank determination was also carried out in the same manner. The % organic matter was then calculated by the equation

$$\% \text{ organic matter} = \frac{(x-y)\ 0.003 \times 100}{2 \times \text{weight of the soil(g)}} \times 1.724 \quad \ldots\ldots(1)$$

Where x and y are the volume (ml) of 0.5 N ferrous ammonium sulfate solution required for blank and sample solution respectively.

IV.2.7 Surface Area: The surface area (A) of the soil sample was determined by the method proposed by Dyal and Hendricks[10]. For this purpose, 2g of the soil sample was taken in a small aluminium box and placed in a dessicator over 250g P_2O_5. The weight of the dried sample was measured. The sample was then wetted with ethylene glycol added from a pipette dropwise and placed in a dessicator at 25±1°C to evaporate excess of ethylene glycol. This sample was weighed several times till a

constant weight was observed. Surface area was then calculated from the equation

$$\text{Surface area } A = \frac{(W_2 - W_1)}{W_1 \times 0.00031} \qquad \ldots\ldots(2)$$

Where W_1 and W_2 are weight (g) of the dried sample and sample wetted with ethylene glycol, respectively and 0.00031 is the Dyal and Hendricks value for the grams of ethylene glycol required to form a monolayer on one m^2 surface area of the soil.

IV.2.8 Effect of Time: The effect of time on the sorption of lead(II) by the soils was studied by taking 1g soil sample with 25 ml of aqueous lead(II) nitrate solution containing 400 µg Pb ml^{-1} in stoppered conical flasks. The flasks were shaken for different time intervals in a temperature controlled SICO shaker at 25±1°C. The suspensions were then centrifuged at 3500 rpm for 10 minutes and lead(II) was determined in the supernatant liquid by atomic absorption spectrometry at 283.3 nm.

IV.2.9 Equilibrium Studies: For equilibrium studies 1g soil sample was taken in different stoppered conical flasks containing varying amounts of pure $Pb(NO_3)_2$ solution and the volume adjusted to 25 ml with distilled

water. The flasks were shaken for two hours at 30±1°C in the first set of experiment and 50±1°C in the second set of experiment, in an electric temperature controlled SICO shaker. The suspensions were then centrifuged at 3500 rpm for 10 minutes and lead(II) was estimated in the supernatant liquid by Atomic Absorption Sepectrometry (GBC 902 Double Beam AAS) at 283.3 nm. Amount of lead(II) sorbed was determined as the difference between the amount of lead(II) added and that left after equilibrium.

The distribution coefficient values (K_d) were determined by using the formula

$$K_d = \frac{I - F}{F} \cdot \frac{\text{Total volume of solution (ml)}}{\text{Weight of the soil (g)}} \quad \ldots.(3)$$

Where I and F are amount of lead(II) added (µg) and that present in the solution after equilibrium, respectively.

The statistical average of all the K_d values was calculated by linear regression equation forced through the origin:

$$K_d = \sum(\frac{x}{m} \cdot Ce) / \sum Ce^2 \quad \ldots.(4)$$

Where x/m is the amount of lead(II) sorbed per gram soil (µg g^{-1}) and Ce, the concentration of lead(II) in equilibrium suspension (µg ml^{-1}).

IV.3 RESULTS

The results of cation exchange capacity, pH, electrical conductance, % organic matter and surface area of both the soils are summerized in Table IV.1.

TABLE - IV.1

Some important properties of the Indian soils

Name of place	pH (1:5)	E.C.x10^{-4} (mho cm^{-1})	O.M. (%)	A (m^2g^{-1})	Cation exchange capacity (mmoles per 100 g)		
					H^+	Ca^{2+}	Pb^{2+}
Aligarh	9.3	4.88	0.37	561.29	5.82	2.80	3.21
Haldighati	6.0	2.20	0.16	960.32	3.88	1.60	2.53

The results of the effect of equilibrium time on the sorption of lead(II) by both the soils are given in Tables IV.2 and IV.3 and plotted in Figure IV.1.

The sorption isotherms of lead(II) on the two soils at different temperatures are plotted in Figure IV.2 and the results of C_e, x/m, $\frac{C_e}{x/m}$, % sorption and K_d values are given in Tables IV.4 and IV.5.

TABLE - IV.2

Effect of equilibrium time on the sorption of lead(II) by Aligarh soil

Equilibrium time (minutes)	µg added, C_o	µg in total suspension	µg sorbed per g soil, x/m
5	10000	7190.0	2810.0
15	10000	6245.0	3755.0
30	10000	5337.5	4662.5
45	10000	4850.0	5150.0
60	10000	4342.5	5657.5
90	10000	3965.0	6035.0
120	10000	3647.5	6352.5
180	10000	3650.0	6350.0
240	10000	3642.5	6357.5

TABLE - IV.3

Effect of equilibrium time on the sorption of lead(II) by Haldighati soil

Equilibrium time (minutes)	µg added, C_o	µg in total suspension	µg sorbed per g soil, x/m
5	10000	7615.0	2385.0
15	10000	6995.0	3005.0
30	10000	6477.5	3522.0
45	10000	5992.5	4007.5
60	10000	5622.5	4377.5
90	10000	5450.0	4550.0
120	10000	5462.5	4537.5
180	10000	5455.0	4545.0
240	10000	5447.5	4552.5

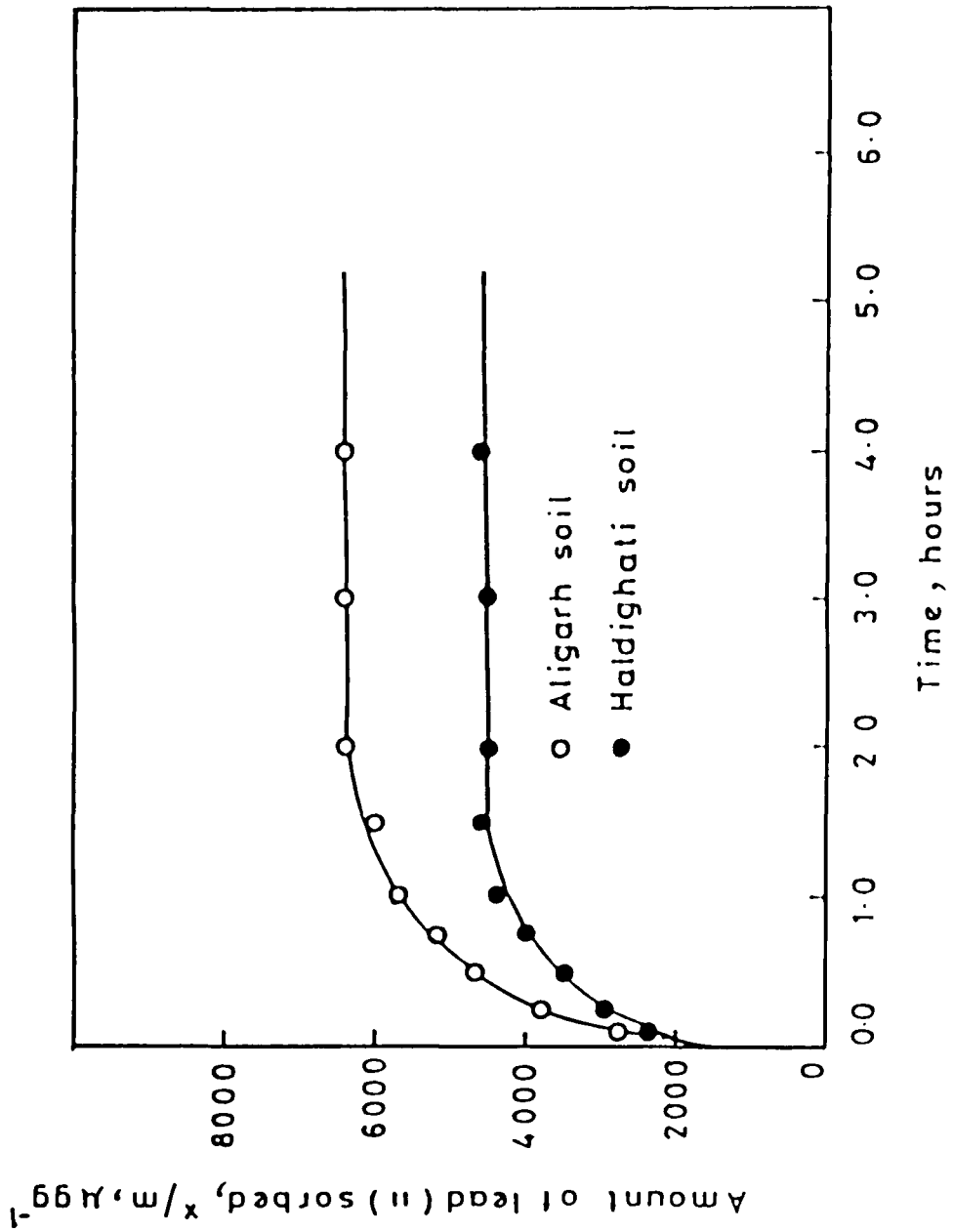

Figure IV.1 Time dependence of sorption of lead(II) on Indian soils

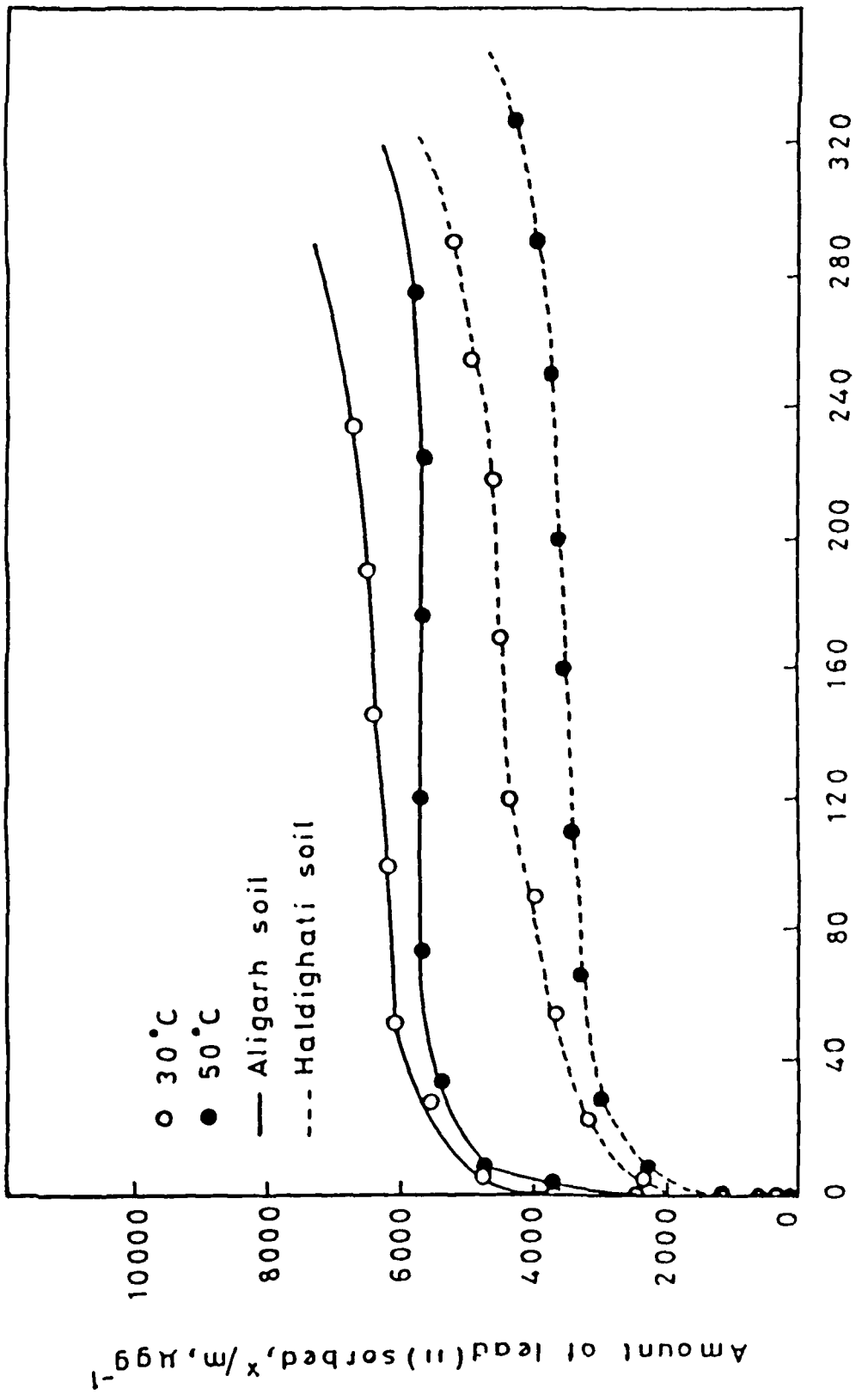

Figure IV.2 Sorption isotherms of lead(II) on Indian soils

TABLE - IV.4

The data for the sorption of lead(II) on Aligarh soil at different temperatures

µg added, C_o	µg in total suspension	Equilibrium concentration, C_e (µg ml^{-1})	µg sorbed per g soil, x/m	$\frac{C_e}{x/m}$	% sorbed	K_d values (ml g^{-1})	Statistical average K_d (ml g^{-1})
			At 30±1°C				
0	0.000	0.000	0.000	0.00	n/a	n/a	
125	0.000	0.000	125.000	0.00	100.00	-E-	
250	0.000	0.000	250.000	0.00	100.00	-E-	
625	0.000	0.000	625.000	0.00	100.00	-E-	
1250	0.150	0.006	1249.850	4.62×10^{-5}	99.99	2.08×10^{5}	
2500	3.850	0.154	2496.150	6.17×10^{-5}	99.85	1.62×10^{4}	31.21
3750	15.875	0.635	3734.125	1.70×10^{-4}	99.58	5.88×10^{3}	
5000	100.125	4.005	4899.875	8.17×10^{-4}	98.00	1.22×10^{3}	
6250	706.500	28.260	5543.500	5.10×10^{-3}	88.70	196.16	
7500	1329.500	53.180	6170.500	8.62×10^{-3}	82.27	116.03	
8750	2486.750	99.470	6236.250	1.59×10^{-2}	71.27	62.69	
10000	3647.500	145.900	6352.500	2.30×10^{-2}	63.53	43.54	
11250	4740.000	189.600	6510.000	2.91×10^{-2}	57.87	34.34	
12500	5850.000	234.000	6650.000	3.52×10^{-2}	53.20	28.42	

Contd...

µg added, C_o	µg in total suspension	Equilibrium concentration, C_e (µg ml^{-1})	µg sorbed per g soil, x/m	$\frac{C_e}{x/m}$	% sorbed	K_d values ($ml\ g^{-1}$)	Statistical average K_d ($ml\ g^{-1}$)
			At 50±1°C				
0	0.000	0.000	0.000	0.00	n/a	n/a	
125	0.000	0.000	125.000	0.00	100.00	-E-	
250	0.000	0.000	250.000	0.00	100.00	-E-	
625	0.250	0.010	624.750	1.60×10^{-5}	99.96	6.24×10^{4}	
1250	2.000	0.080	1248.000	6.41×10^{-5}	99.84	1.56×10^{4}	
2500	10.050	0.402	2489.950	1.61×10^{-4}	99.60	6.19×10^{3}	
3750	38.875	1.555	3711.125	4.19×10^{-4}	98.96	2.39×10^{3}	28.87
5000	147.625	5.905	4852.375	1.22×10^{-3}	97.05	821.74	
6250	850.750	34.030	5399.250	6.30×10^{-3}	86.39	158.66	
7500	1821.500	72.860	5678.500	1.28×10^{-2}	75.71	77.94	
8750	3022.500	120.900	5727.500	2.11×10^{-2}	65.46	47.37	
10000	4410.000	176.400	5590.000	3.16×10^{-2}	55.90	31.69	
11250	5602.500	224.100	5647.500	3.97×10^{-2}	50.20	25.20	
12500	6850.000	274.000	5650.500	4.85×10^{-2}	45.20	20.29	

TABLE - IV.5

The data for the sorption of lead(II) on Haldighati soil at different temperatures

µg added, C_o	µg in total suspension	Equilibrium concentration, C_e(µg ml^{-1})	µg sorbed per g soil, x/m	$\frac{C_e}{x/m}$	% sorbed	K_d values ($ml\ g^{-1}$)	Statistical average K_d ($ml\ g^{-1}$)
			At 30±1°C				
0	0.000	0.000	0.000	0.00	n/a	n/a	
125	0.000	0.000	125.000	0.00	100.00	-E-	
250	0.000	0.000	250.000	0.00	100.00	-E-	
625	0.000	0.000	625.000	0.00	100.00	-E-	
1250	0.000	0.000	1250.000	0.00	100.00	-E-	
2500	145.900	5.836	2354.100	2.48×10^{-3}	94.16	403.38	22.67
3750	565.375	22.615	3184.625	7.10×10^{-3}	84.92	140.82	
5000	1360.000	54.400	3640.000	1.49×10^{-2}	72.80	66.91	
6250	2236.750	89.470	4013.250	2.22×10^{-2}	64.21	44.86	
7500	3027.500	121.100	4472.500	2.71×10^{-2}	59.63	36.93	
8750	4275.000	171.000	4475.000	3.82×10^{-2}	51.14	26.17	
10000	5450.000	218.000	4550.000	4.79×10^{-2}	45.50	20.87	
11250	6357.500	254.300	4892.500	5.20×10^{-2}	43.49	19.24	
12500	7252.500	290.100	5247.500	5.53×10^{-2}	41.98	18.09	

Contd...

µg added, C_o	µg in total suspension	Equilibrium concentration, C_e (µg ml^{-1})	µg sorbed per g soil, x/m	$\frac{C_e}{x/m}$	% sorbed	K_d values (ml g^{-1})	Statistical average K_d (ml g^{-1})
			At 50±1°C				
0	0.000	0.000	0.000	0.00	n/a	n/a	
125	0.000	0.000	125.000	0.00	100.00	-E-	
250	0.000	0.000	250.000	0.00	100.00	-E-	
625	0.000	0.000	625.000	0.00	100.00	-E-	
1250	25.100	1.004	1224.900	8.20×10^{-4}	97.99	1.22×10^{3}	
2500	180.800	7.232	2319.200	3.12×10^{-3}	92.77	320.69	
3750	710.125	28.405	3039.875	9.34×10^{-3}	81.06	107.02	12.46
5000	1650.000	66.000	3350.000	1.97×10^{-2}	67.00	50.76	
6250	2850.000	114.000	3400.000	3.35×10^{-2}	54.40	29.82	
7500	4000.000	160.000	3500.000	4.75×10^{-2}	46.67	21.88	
8750	6157.000	206.300	3592.500	5.74×10^{-2}	41.06	17.41	
10000	6292.500	251.700	3707.500	6.79×10^{-2}	37.08	14.73	
11250	7285.000	291.400	3965.000	7.35×10^{-2}	35.24	13.61	
12500	8152.500	326.100	4347.500	7.50×10^{-2}	34.78	13.33	

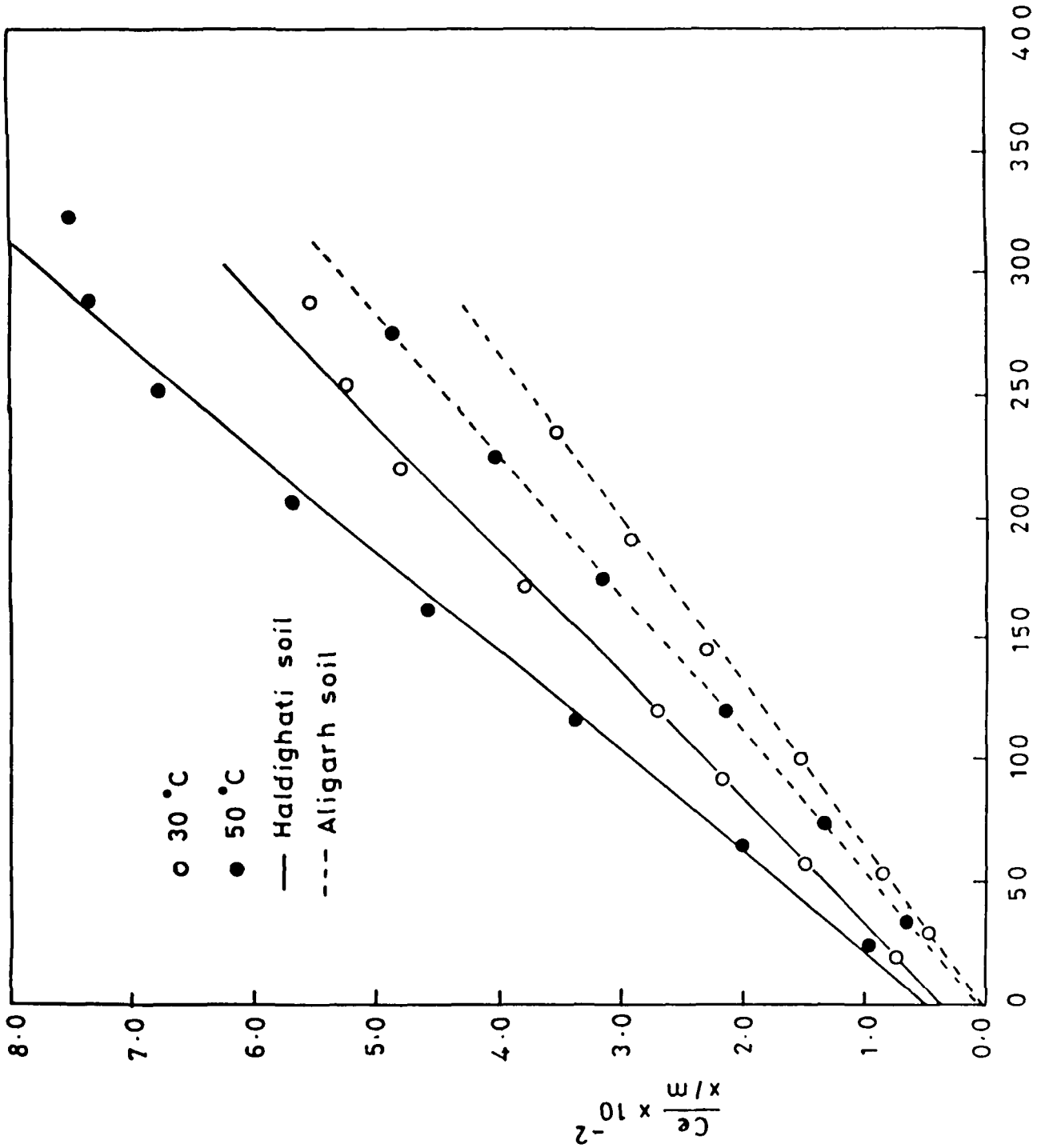

Figure IV.3 Test of Langmuir isotherm for lead(II) on Indian soils

The plots of $\frac{C_e}{x/m}$ versus C_e for the two soils are presented in Figure IV.3 and the values of Langmuir constants K and b are given in Table IV.6.

TABLE - IV.6

Langmuir constants, K and b at different temperatures

Name of place	30°C		50°C	
	K	b $\mu g\ g^{-1}$	K	b $\mu g\ g^{-1}$
Aligarh	0.7709	6.486×10^3	0.3473	5.758×10^3
Haldighati	0.0552	5.172×10^3	0.0376	4.211×10^3

The plots of $\ln \frac{C_s}{C_e}$ versus C_s for the two soils are presented in Figures IV.4 and IV.5. The thermodynamic equilibrium constant K_o obtained from these plots are given in Table IV.7. The enthalpy change was evaluated from the plots of $\ln K_o$ versus 1/T (Figure IV.6). The free energy change and entropy change were calculated by using appropriate equations. The values of various thermodynamic parameters are summarized in Table IV.7.

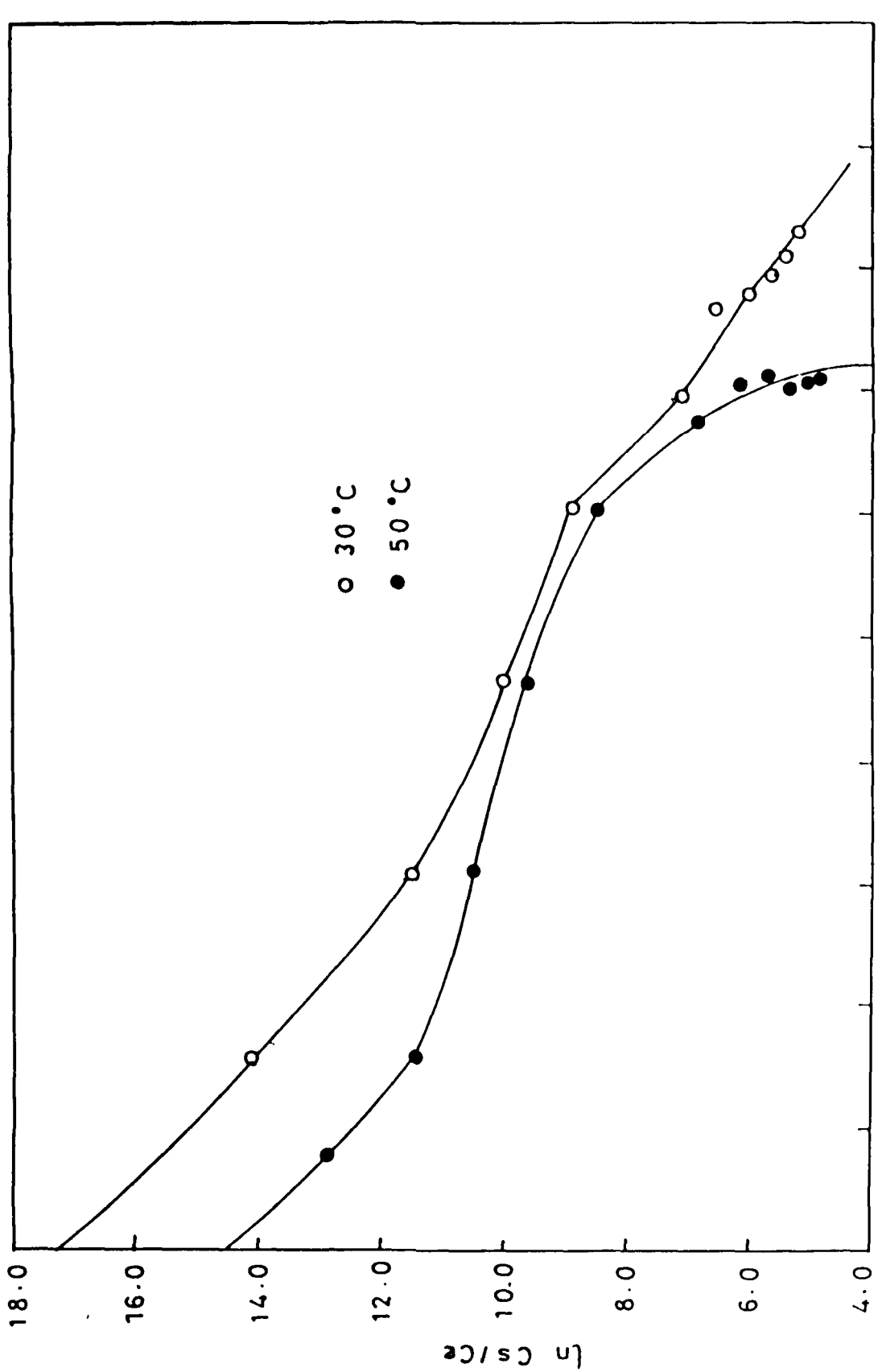

Figure IV-4 Plots of ln C_s/C_e versus C_s of lead(II) in Aligarh soil

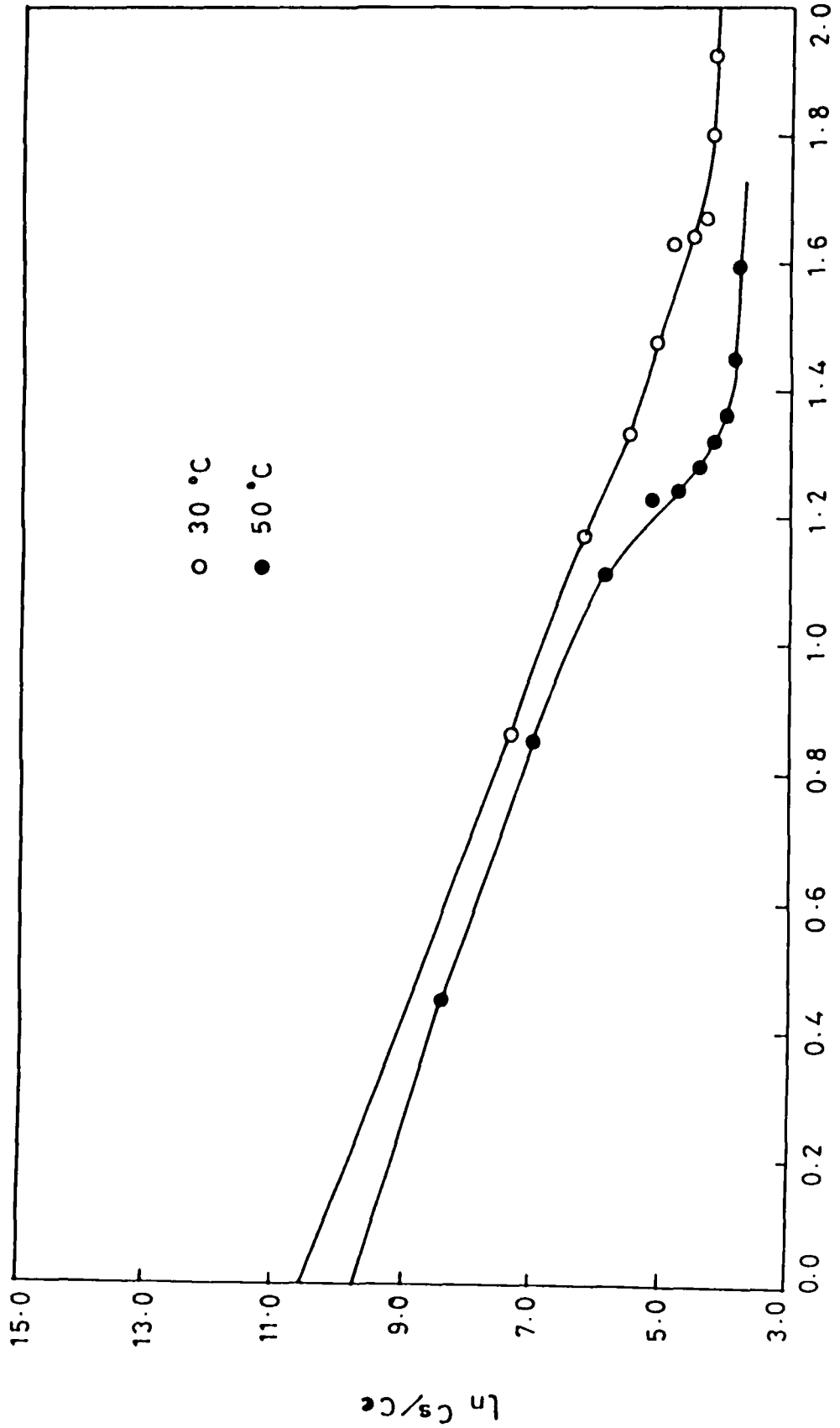

Figure IV.5 Plots of ln C_s/C_e versus C_s of lead(II) in Haldighati soil

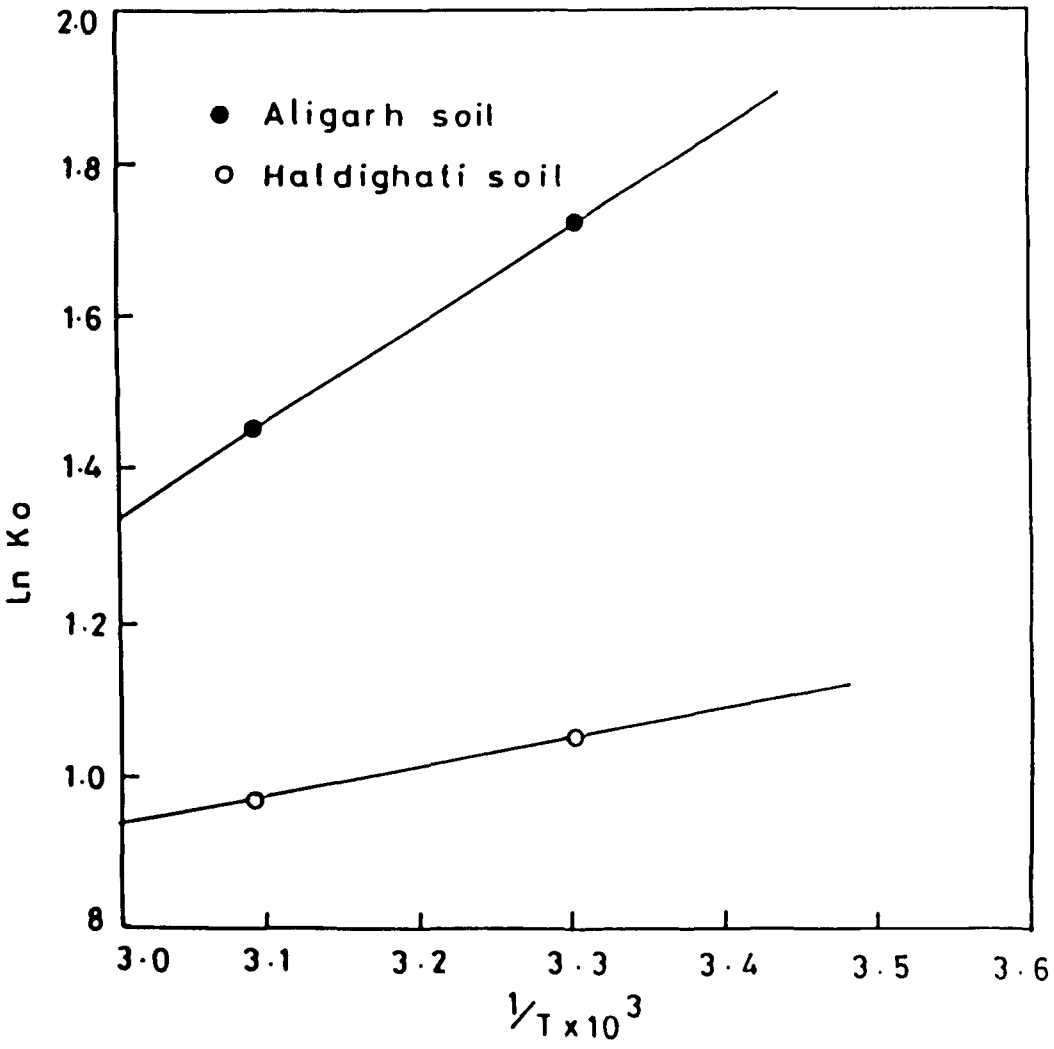

Figure IV.6 Determination of enthalpy of sorption of lead(II) on Indian soils

TABLE - IV.7

Various thermodynamic parameters for the sorption of lead(II) on the Indian soils

Thermodynamic parameters	Aligarh soil		Haldighati soil	
	30°C	50°C	30°C	50°C
K_o	2.95×10^7	1.98×10^6	3.63×10^4	1.63×10^4
$\Delta G°$ (KJ mol^{-1})	-43.35	-38.96	-26.47	-26.06
$\Delta H°$ (KJ mol^{-1})	-109.96		-32.58	
$\Delta S°$ (KJ $K^{-1} mol^{-1}$)	-0.2197	-0.2197	-0.0202	-0.0202

IV.4 DISCUSSION

It is evident from Table IV.1 that the two Indian soils varied widely in their properties. The pH, electrical conductance and organic matter content of Aligarh soil were greater than that of Haldighati soil. The Aligarh soil shows higher cation exchange capacity than the Haldighati soil. This may be attributed to greater amount of organic matter present in Aligarh soil.

The results of the effect of equilibrium time on the sorption of lead(II) by the two soils (Tables IV.2 and IV.3, Figurre IV.1) show that the sorption of lead(II) on both the soils increased with the increase in time of equilibrium upto a certain time, after that became constant at two hours for Aligarh soil and one and half hours for Haldighati soil. Therefore these periods were chosen for sorption studies of lead(II) on the two soils.

Sorption of lead(II) was studied by batch process in the concentration range, 0-234 $\mu g\ ml^{-1}$ and 0-274 $\mu g\ ml^{-1}$ at 30 and 50°C, respectively for Aligarh soil and 0-290 $\mu g\ ml^{-1}$ and 0-326 $\mu g\ ml^{-1}$ at 30 and 50°C,

respectively for Haldighati soil. Sorption isotherms were plotted between the amount of lead(II) sorbed per gram soil (ug g^{-1}) and the amount of lead(II) in equilibrium suspension (ug ml^{-1}). It is clear from Figure IV.2 that sorption of lead(II) was higher on Aligarh soil than Haldighati soil. The higher sorption of lead(II) on Aligarh soil could be due to the greater amount of organic matter and higher cation exchange capacity. The sorption of lead(II) decreases with the rise in temperature in both the soils partly due to the weakening of attractive forces between lead(II) and soil and partly due to enhancement of thermal energies of the adsorbate; thus making the attractive force between lead(II) and soil weaker for the sorption of lead(II) at the binding sites.

From sorption data, the distribution coefficient values for the ion exchange/sorption of lead(II) on both the soils were calculated using equations 3 and 4. The K_d values (Tables IV.4 and IV.5) also confirm higher sorption of lead(II) on Aligarh soil. Percent sorption and statistical average of all the K_d values (Tables IV.4 and IV.5) show the same order for the sorption of lead(II) on both the soils.

An examination of Figure IV.2 reveals that the sorption isotherms at both the temperatures are of 'H' class[11] for both the soils. These isotherms result from strong sorption at low concentrations giving an apparent intercept on the ordinate. The shape of the isotherms suggest that the interaction between lead(II) ions was negligible and therefore the energy of activation for removal of lead(II) from surface was independent of coverage[12,13].

The sorption behaviour of lead(II) in both the soils was in close agreement with the linear form of the Langmuir equation[14]

$$\frac{C_e}{x/m} = \frac{1}{K\,b} + \frac{C_e}{b} \qquad \ldots\ldots(5)$$

Where K and b are constants which represent the binding energy coefficient and sorption maxima, respectively.

By plotting $\frac{C_e}{x/m}$ against C_e (Figure IV.3) a straight line was obtained for both the soils. Langmuir constants K and b were evaluated from the intercept and slope of these plots respectively. The results given in Table IV.6 show higher values of Langmuir constants

for Aligarh soil than Halidghati soil at both the temperatures. These results also confirm higher sorption of lead(II) in former. Similarly, higher values of the constants at 30°C also suggest higher sorption of lead(II) on both the soils at lower temperature. These results are in accordance with those of Veith and Sposito[15], who studied the use of Langmuir equation in the interpretation of adsorption phenomena and with those of Harter[6] regarding the adsorption of lead and copper by the soils of Northern United States. Although, sorption process is primarily one of cation exchange, the Langmuir equation has been frequently applied to the sorption of heavy metal cations from solution by the soils[6].

The thermodynamic equilibrium constant (K_o) for the sorption of lead(II) on the soils was calculated by Biggar and Cheung[16] method as applied by Singh et al.[17]

$$K_o = \frac{C_s}{C_e} \cdot \frac{\nu_s}{\nu_e} \qquad \ldots\ldots(6)$$

Where C_s ($\mu g\ g^{-1}$) is the amount of lead(II) adsorbed per gram of the solvent in contact with the soil, C_e ($\mu g\ ml^{-1}$) the concentration of lead in equili-

brium suspension, ν_s the activity coefficient of the adsorbed solute and ν_e the activity coefficient of the solute in equilibrium suspension.

The value of C_s was calculated by using the equation proposed by Fu et al.[18]

$$C_s = \frac{(\varrho/M)\ A}{S/N\ (x/m)} \qquad ....(7)$$

Where ϱ is the density of the solvent (g ml^{-1}), M the molecular weight of the solvent, A the cross sectional area of the solvent molecule (cm^2 $molecule^{-1}$), N the Avogadro's number, S the surface area of the adsorbent (m^2 g^{-1}) and x/m the specific adsorption (m.mol g^{-1}).

The cross sectional area of the solvent molecule was calculated by using the equation[19]

$$A = 1.091 \times 10^{-16} \left(\frac{10^{24}\ M}{N\varrho}\right)^{2/3} \qquad ....(8)$$

The ratio of the activity coefficient was assumed to be unity in the dilute range of studies[20]. As the concentration of solute in the solution approached zero, the activity coefficient approached unity. Equation 6 may then be written as -

$$\lim_{C_s \to 0} \frac{C_s}{C_e} = K_o \qquad \ldots(9)$$

The values of K_o were obtained by plotting $\ln C_s/C_e$ versus C_s and extrapolating to zero C_s (Figures IV.4 and IV.5).

From the values of thermodynamic equilibrium constant, free energy changes ($\Delta G°$) during the sorption/ ion exchange phenomena were calculated from the relationship[21]

$$\Delta G° = - RT \ln K_o \qquad \ldots(10)$$

Where R is universal gas constant and T the absolute temperature.

The enthalpy change ($\Delta H°$) was calculated by using the integrated form of the Van't Hoff equation

$$\ln \left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{-\Delta H°}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ldots(11)$$

The $\Delta H°$ value was evaluated from the plots of $\ln K_o$ versus 1/T (Figure IV.6) and the entropy changes ($\Delta S°$) were calculated from $\Delta H°$ and $\Delta G°$ values using the equation -

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \qquad \ldots.(12)$$

The values of thermodynamic equilibrium constant, free energy changes, enthalpy change and entropy changes, at 30 and 50°C for the sorption of lead(II) on both the soils are summarized in Table IV.7. These results show higher value of K_o at 30°C than at 50°C for both the soils indicating higher preference of lead(II) by the soils at lower temperature. However, these values were higher for Aligarh soil than Haldighati soil, which again confirm that sorption of lead(II) was higher in former, at both the temperatures. The results (Table IV.7) show negative values of ΔG° for the sorption of lead(II) on the soils at both the temperatures. It is clear from these results that enthalpy change ΔH° is also negative which indicates that sorption of lead(II) on the soils was exothermic and a decrease in temperature favoured the reaction. The results of ΔH° values together with that of ΔG° values confirm that ion exchange/sorption process had a natural tendency to proceed spontaneously. More negative value of ΔH° for Aligarh soil confirms that lead(II) was more strongly bound to Aligarh soil as compared to Haldighati soil. The results of entropy change (Table IV.7) show a loss

in entropy, more during the sorption of lead(II) on Aligarh soil; indicating a greater order produced during the sorption/ion exchange phenomena. The negative values of entropy change suggest that there was a reduction in translational freedom when the solute was sorbed.

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Chapter V

Redox Ion Exchanger Fuel Cell

V.1 INTRODUCTION

Our conventional sources of energy, such as fossil fuels, hydroelectricity and nuclear energy, each has its own limitations and associated hazards. This necessitates the development of sources of energy other than the conventional ones. The possibility of finding new sources of energy has been highlighted recently in our country.[1] Much emphasis has been given to research needs for advanced fuel cells.[2] Its technology and applications have also been studied.[3]

In general a hydrogen/oxygen fuel cell is used in which electrodes are made of titanium coated with platinum and the electrolyte is a cation exchange resin.[4] Oxygen is normally the oxidant and hydrogen is most widely used fuel. The energy producing reaction is the oxidation of hydrogen by oxygen.

Ion exchangers have been widely used as an electrolyte in fuel cells. Fugita et al.[5] have made a fuel cell in which a combined body of cation exchange membrane electrolyte between two electrodes had porous collector of sintered Ti fibers pressed on electrodes. A sulfonated perfluorocarbon cation exchange membrane

was coated with Pt to form a cathode on one side and with Rh on the other side to form anode. Mucoyama and Hirai[6] made fuel cells using electrolytes which were prepared from particles of strongly acid cation exchange resin. The resin particles were made into paste with the addition of water and SiC powder and filled into the cavity between the fuel (MeOH) anode and an ion exchange membrane covering the oxidant (air) cathode. A fibrous ion exchanger sheet has been used as an electrolyte in a fuel cell prepared by Mitsubishi Rayon Co. Ltd. Japan.[7] The fibrous cation exchanger bonded on a Ni mesh core to prepare an electrolyte was sandwiched between an anode and a cathode. Kummer and Oei[8] prepared a chemically regenerative redox fuel cell in which a suitable cation exchange memberane was housed in a housing provided with openings on opposite sides of the membrane for the catholyte and anolyte respectively so that necessary exchange may take place to form a redox cell.

The present work was undertaken to study the usefulness of a redox reaction between Fe^{3+} and Zn on an ion exchanger bed for the preparation of a fuel cell. A comprehensive review of the literature reveals that Zn^{2+}/Zn and Fe^{2+}/Fe^{3+} system has not been used for the

preparation of redox ion exchanger fuel cells so far. The system in question has been chosen because of a significant difference between the electrode potentials of Zn^{2+}/Zn and Fe^{2+}/Fe^{3+} couples. Moreover, the system becomes further important owing to its low cost, easy availability and the ease with which the redox ion exchanger can be prepared ie. simply by incorporating Fe^{3+} ion in an easily available cation exchange resin (e.g. Dowex 50 W X 8). The redox ion exchanger so formed can be regenerated after use. Most of the ion exchanger fuel cells reported in literature[5-8] suffer from several shortcomings. Their assemblies are either too complicated hence need sophosticated operators, or the procedures for making them are cumbersome. Our redox ion exchanger fuel cell (REFC) requires a very simple assembly and the operation is very easy yet it furnishes a voltage of 0.69 ± 0.05 V which is comparable with the magnitude of voltage obtained from other fuel cells using ion exchangers.

V.2 EXPERIMENTAL

V.2.1 Electrode Material for REFC: In the present investigation a redox ion exchanger has been used for the construction of the electrode. Redox ion exchanger was prepared from Dowex 50 W X 8 cation exchange resin by replacing the counter ion by Fe^{3+} ion.[9] Standard electrode potential of the couple Fe^{2+}/Fe^{3+} is little affected by incorporation of the couple into the ion exchanger.[10] Dowex 50 W X 8 was kept in one molar solution of ferric nitrate for 24 hours then it was washed thoroughly with distilled water and was dried at 30±1°C. The resulting redox ion exchanger was packed in a glass tube narrow at one end fitted with glass wool.

V.2.2 Design and Working of REFC: Redox ion exchanger (5 g) packed in a glass tube worked as cathode while zinc metal was used as anode. Both the electrodes were dipped in a beaker containing one molar solution of zinc nitrate (50 ml). Connections were made through a copper wire. Although platinum wire gives better results, the use of copper wire is recommended to keep the cost low. A multimeter was used for voltage and current measurements. A schematic diagram of the REFC is given in Figure V.1.

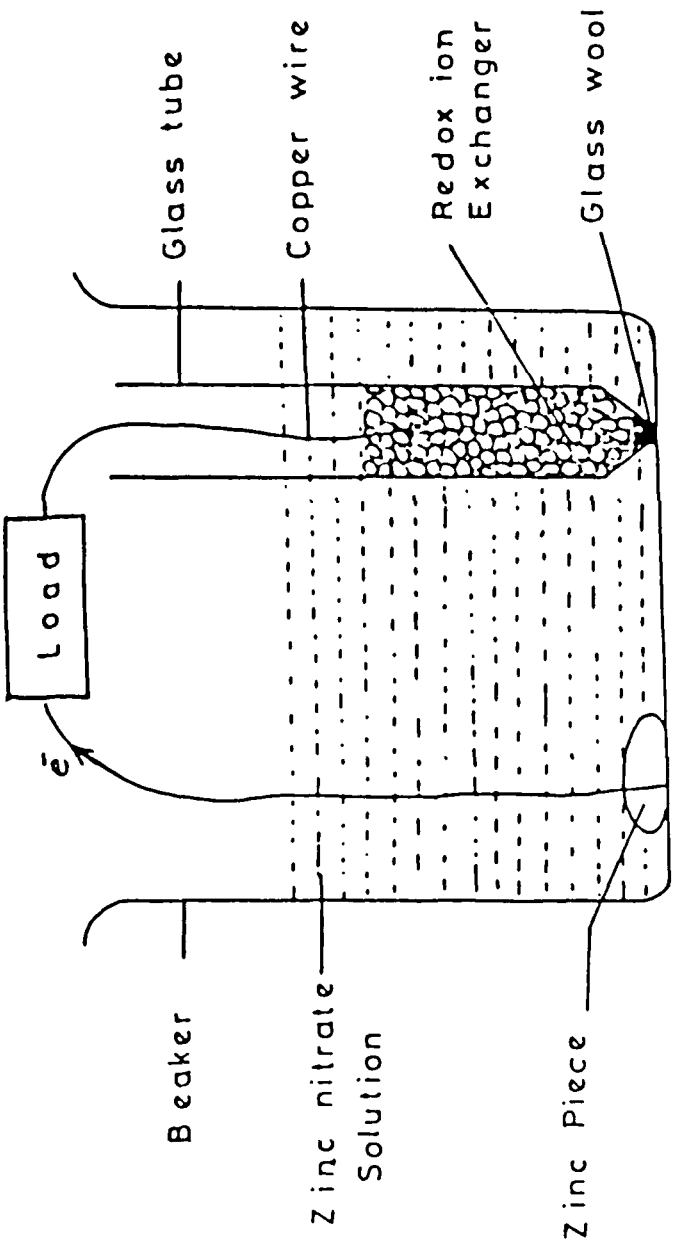

Figure V.1 A redox ion exchanger fuel cell

The concentration of zinc nitrate solution was kept constant at one molar and that of Fe^{3+} ion in the redox exchanger at one molal, to maintain standard conditions. Electrode potentials were calculated using Nernst equation. Electrode potentials of the couples Fe^{2+}/Fe^{3+} and Zn^{2+}/Zn were found to be +0.771 volts and -0.763 volts respectively. Since electrode potential of the couple Zn^{2+}/Zn is lower than that of the couple Fe^{3+}/Fe^{2+}, the former is oxidised and furnishes electrons to the latter. The energy producing reaction is oxidation of the substrate by the redox ion exchanger.

$$Zn \rightleftharpoons Zn^{2+} + 2e^{-} \qquad \text{at anode..... (1)}$$

$$2Fe^{3+} + 2e^{-} \rightleftharpoons 2Fe^{2+} \qquad \text{at cathode... (2)}$$

so that net reaction is

$$Zn + 2Fe^{3+} \rightleftharpoons Zn^{2+} + 2Fe^{2+} \qquad \text{..... (3)}$$

V.3 RESULTS

From a single cell, a voltage of 0.69 ± 0.05 V and 370 ± 70 μA current was obtained. Voltage and current data for six similar redox ion exchanger fuel cells are summarized in Table V.1.

TABLE - V.1

Voltage and current data for six similar redox ion exchanger fuel cells

Cell No.	Voltage V	Current mA	Standard deviation		Relative standard deviation	
			For voltage V	For current mA	For voltage %	For current %
1	0.64	0.42	0.027 absolute value	0.037 absolute value	3.92	10.00
2	0.72	0.34				
3	0.70	0.34				
4	0.68	0.34				
5	0.70	0.41				
6	0.69	0.38				

The magnitude of the current and voltage of the redox ion exchanger fuel cell was increased by connecting the cells in series and parallel. The results are summarized in Table V.2.

TABLE - V.2

Increase in voltage and current on connecting the redox ion exchanger fuel cells in series and parallel

Type of connection	Number of cells	Theoretical value		Experimental value	
		Voltage V	Current mA	Voltage V	Current mA
(a) Series	2	1.38	0.37	1.22	0.36
	4	2.76	0.37	2.43	0.37
(b) Parallel	2	0.69	0.74	0.68	0.68
	4	0.69	1.48	0.66	1.30

V.4 DISCUSSION

For six redox ion exchanger fuel cells voltage and current measurements were made individually. It is clear from Table V.1 that the value of voltage varies from 0.64 to 0.72 V whereas the value of current lies within 340 to 420 μA range. The voltage was taken as a steady state voltage. Standard and relative standard deviations for voltage and current measurements were also computed (Table V.1). These results show the reproducibility of the redox ion exchanger fuel cell.

The magnitude of the voltage was increased additively by connecting more cells in series. For example when four cells were connected in series a voltage of 2.43 V was obtained which is in good agreement with a theoretically expected value of 2.76 V (Table V.2). The theoretical value of voltage for four cells in series is simply four times the voltage due to a single cell. A little discrepancy seen between the observed and theoretically predicted value may be attributed to experimental errors. The same arrangement of four cells in series furnishes a current of 370 μA which is sufficient enough to display an electronic calculator. When the cells are connected in parallel

the current increases additively. Table V.2 shows that on connecting four cells in parallel 1.30 mA current is obtained which is approximately four times the current due to a single cell. The experimental value is in agreement with the theoretical value (1.48 mA). A fuel cell system consists of fuel cell stacks connected in parallel[11].

One difficulty was observed with this redox ion exchanger fuel cell that an internal reistance is produced on loading the cell (Figure V.2). As a result there was a voltage drop in the cell and somewhat lesser voltage was available to the load. However, internal resistance can be minimized by connecting more cells in parallel.

The number of fuel cells required to obtain 10 mA current were calculated. The voltage obtained from four cells connected in series, without loading was 2.43 V. On connecting a 1.5 V bulb (load) there was a voltage drop and only 1.515 V were available to the load.

Therefore voltage drop = 2.43 V - 1.515 V

= 0.915 V

Current measured = 370 μA = 370x 10^{-6}A

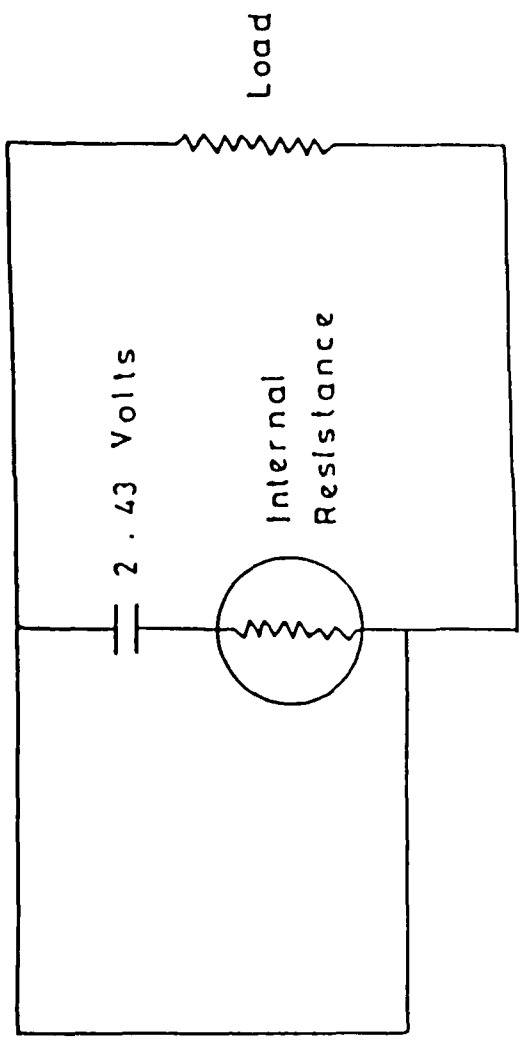

Figure V.2 Circuit diagram of REFC showing internal resistance

$$\therefore \text{ Internal resistance} = \frac{0.915\ V}{370 \times 10^{-6} A}$$

$$= 2472.97 \text{ Ohm}$$

Since current required is 10 mA, the resistance should be minimized to a value

$$= \frac{0.915\ V}{10 \times 10^{-3} A}$$

$$= 91.5 \text{ Ohm}$$

Now number of fuel cell stacks connected in parallel

$$= \frac{2472.97 \text{ Ohm}}{91.5 \text{ Ohm}}$$

$$= 28$$

Where each fuel cell stack consists of four cells connected in series.

The theoretical calculations suggest that 112 cells are required to obtain 10 mA current. There are 28 such fuel cell stacks and all these 28 fuel cell stacks should be connected in parallel. The resulting fuel cell system can furnish a voltage equal to 2.43 volts and 10 mA current. Although, these calculations are purely theoretical and have not been put to any experimental test, they may give an idea about the number

of cells required to obtain 10 mA current.

Redox ion exchanger fuel cells have many advantages over others such as their low cost, pollution free operation, regenerative nature and easy reaction conditions. However, they require further improvements in current, voltage output and need to be more compact for their development.

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Synthesis and Ion Exchange Properties of Sodium Stannosilicate: A Silver Selective Inorganic Ion Exchanger

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An inorganic ion exchanger sodium stannosilicate has been synthesized. Its composition, chemical and thermal stabilities and ion exchange properties have been studied. This material is obtained as hard granules and is very stable at high temperatures. Its ion exchange capacity for Ag^+ is 2.25 mequiv g^{-1}. The material shows high selectivity towards Ag^+ which has been separated quantitatively from Pb^{2+}, Hg^{2+}, and Cu^{2+}. Recovery of Ag^+ from dilute solutions has also been studied.

The use of synthetic inorganic ion exchangers is successfully being developed for the selective separation of a number of metal ions. New materials are being synthesized[1-4] to solve such specific problems. There is a revived interest towards the ion exchange properties of silicates.[5-9] Zeolites have been extensively studied for its ion exchange properties particularly by Barrer.[10] Desai and Baxi have studied ion exchange properties of tin silicate.[6]

The present paper reports the synthesis, chemical composition, chemical and thermal stabilities, and ion exchange properties of sodium stannosilicate, an analogue of the zeolites. This material shows higher exchange capacity and is more stable at high temperatures than tin silicate prepared at pH 8.5. The distribution ratios for different metal ions have revealed that the exchanger is specific towards Ag^+. K_d values for other metal ions are also higher for sodium stannosilicate than those for tin silicate. The utility of this material has been studied for the separation of Ag^+ from other metal ions and its recovery from dilute solutions.

Experimental

Reagents: Tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) (Reachim) and sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) (Loba) were used. All other chemicals used were of A. R. grade.

Apparatus: An electric temperature controlled SICO shaker and Bausch and Lomb spectronic-20 (U.S.A.) were used for shaking and spectrophotometric determinations respectively. Elico pH meter model Li-10 (India) was used for pH measurements.

Preparation of Sodium Stannate Solution: Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) was prepared by mixing 0.5 M sodium hydroxide solution (1 M=1 mol dm^{-3}) to 0.1 M tin(IV) chloride solution.[11] The pH was adjusted to 10 by adding sodium hydroxide solution. The solution initially turbid, turned into a clear solution of sodium stannate on heating at 60 °C.

Synthesis of Sodium Stannosilicate: Sodium stannosilicate was synthesized by mixing 0.1 M sodium metasilicate solution with 0.1 M sodium stannate solution in 1:1 volume ratio. The yield of sodium stannosilicate in other mixing volume ratios was very low. Therefore 1:1 volume ratio was chosen for synthesis. The resulting mixture was refluxed for 24 hours. The white precipitate obtained was allowed to settle overnight, washed with distilled water and dried at 60 °C. The dried product was immersed in distilled water when it broke down easily into small granules. It was washed several times with distilled water and then dried in an air oven at 60 °C.

Cation Exchange Capacity: Ion exchange capacity for H^+ ion was determined by taking sodium stannosilicate in H^+ form and then eluting with 1.0 M sodium nitrate solution. Metal ion capacity was determined by shaking 1.0 g of the exchanger with 50 ml 0.1 M aqueous solution of metal nitrate at 25 °C and titrating the metal ion left in the supernatant liquid.

Chemical Stability: The chemical stability of sodium stannosilicate was studied in different solvents. For this purpose 100 mg of the exchanger was shaken with 25 ml of the appropriate solvent for 6 hours at 25 °C. The amount of silica released in the supernatant liquid was determined by a standard colorimentric method.[12]

Chemical Composition: A 200 mg portion of sodium stannosilicate was dissolved in 200 ml solution containing 15 ml of sulfuric acid and 100 ml of hydrochloric acid. Tin in this sample was reduced by zinc powder and determined iodometrically.[13] For the determination of silicon a 200 mg portion of the exchanger was heated in 200 ml solution containing 100 ml of hydrochloric acid. Silicon was precipitated as silicic acid. It was ignited in a platinum crucible and weighed as SiO_2.[14]

Thermal Stability: Sodium stannosilicate (0.5 g) was weighed in different silica crucibles and dried at different temperatures in a muffle furnace for 2 hours. Exchange capacity for Ag^+ was determined for the products dried at 60, 100, 150, 200, and 250 °C. Weight loss was also calculated at the respective temperatures.

Hydrolysis: Sodium stannosilicate was taken in H^+ and Na^+ forms. The exchanger (0.5 g) was shaked with 25 ml of distilled water at 25 °C for different time intervals. The pH of the supernatant liquid was measured after each time-interval.

Water Sorption: Sodium stannosilicate (1.0 g) in different ionic forms was equilibrated with 20 ml of distilled water for 1 hour at 25 °C. Sodium stannosilicate was then separated from water and weighed in a stoppered weighing bottle. It was then dried over a dessicant in vaccum at 60 °C and reweighed. Amount of water sorbed by sodium stannosilicate was calculated from the difference between the wet weight and dry weight.

IR Analysis: IR spectrum of the material dried at 60 °C

was obtained using KBr disc technique on an IR-20 spectrometer.

Distribution Coefficients: Sodium stannosilicate (0.5 g) was shaken with 50 ml of 0.02 M solution of the metal nitrate for 6 hours at 25 °C. The supernatant liquid was titrated for the determination of metal ion left. Silver was determined by titration with 0.02 M KSCN solution. All other cations were determined by titration with 0.02 M solution of EDTA. The K_d values of these ions were determined in aqueous solution.

Distribution coefficient values for a number of metal ions on sodium stannosilicate were calculated from the relationship

$$K_d = \frac{I - F}{F} \times \frac{V}{W}.$$

Where I and F are initial and final volumes of titrant before and after equilibration. V is volume of the metal ion solution and W is weight of the exchanger.

Column Separations: A glass column (length 45 cm, diameter 0.39 cm) was filled to a height of 14 cm with 2.0 g of the exchanger on a glass wool support. The column was washed with 10 bed volumes of distilled water. The aqueous mixture solution (10 ml) containing the metal ions to be separated was passed onto the column at a slow rate. The column was again washed with distilled water. The metal ions were then eluted by passing a suitable eluent. The eluent was passed at a flow rate of 0.2 ml min^{-1}. The metal ions in 10 ml fractions of effluent were collected and determined titrimetrically.

Recovery of Ag^+: Uptake of Ag^+ by sodium stannosilicate was studied from silver nitrate solution of different concentrations. Sodium stannosilicate (0.5 g) was shaked with 50 ml of silver nitrate solution at 25 °C for 6 hours. The supernatant liquid was titrated for the determination of Ag^+ left.

Uptake of Ag^+ from solutions containing sodium ion was also studied. Sodium stannosilicate (0.5 g) was added to 50 ml of 0.02 M silver nitrate solution containing equal amounts of sodium nitrate and shaked for 6 hours at 25 °C. The supernatant liquid was titrated for the determination of Ag^+ left.

Table 1. Exchange Capacity of Sodium Stannosilicate

Serial No.	Cation	Exchange capacity (mequiv g^{-1})
1	H^+	0.23
2	Ag^+	2.25
3	Mg^{2+}	0.80
4	Ca^{2+}	1.00
5	Cu^{2+}	1.20
6	Co^{2+}	0.90
7	Mn^{2+}	1.00
8	Hg^{2+}	1.44
9	Pb^{2+}	1.20
10	Cd^{2+}	1.10

Results and Discussion

From the results given in Table 1 it can be inferred that sodium stannosilicate works as an extremely weak cation exchanger and releases a small amount of hydrogen ions. The metal ion capacity is sufficiently high and varies from 0.8 to 2.25 mequiv g^{-1}.

Table 2 shows the stability of sodium stannosilicate in different solvents. The values in the table show that sodium stannosilicate can be used in nearly neutral media i.e. water, salt solutions, alcohols, dilute acids, and alkali without any appreciable loss. The results of thermal stability show that there is a slight (3.7%) weight loss at 100 °C and 8.12% weight loss at 150 °C; no further weight loss is observed up to 250 °C. The maximum capacity for Ag^+, however, remains contant throughout the temperature range studied. These

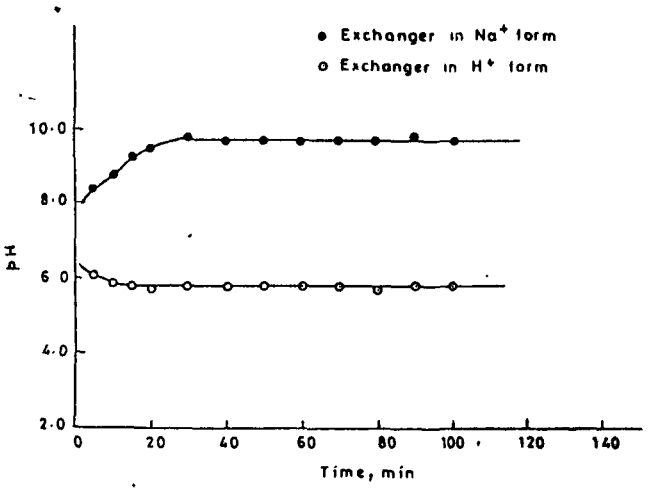

Fig. 1. Hydrolysis curves for sodium stannosilicate.

Table 2. Chemical Stability of Sodium Stannosilicate in Different Solvents[a]

Serial No.	Solvent	Amount of silica released (mg/25 ml)
1	Distilled water	0.00
2	Nitric acid, 0.1 M	0.127
3	Hydrochloric acid, 0.1 M	0.127
4	Sulfuric acid, 0.1 M	0.165
5	Ethanol	0.00
6	Sodium acetate, 1 M	0.00
7	Sodium hydroxide, 0.1 M	0.185
8	Sodium nitrate, 1 M	0.00
9	Sodium citrate, 1 M	0.00

a) Amount of sodium stannosilicate taken=100 mg.

results suggest that only hydration water is released by heating up to 150 °C and no structural changes take place.

The chemical analysis of the exchanger sodium stannosilicate shows that the apparent ratio of Sn : Si is 1:1. The results of hydrolysis plotted in Fig. 1 show that sodium stannosilicate hydrolyses appreciably. When sodium stannosilicate is in Na^+ form there is a gradual increase in pH for up to 30 minutes, thereafter, pH remains almost constant. On the other hand, when sodium stannosilicate is in H^+ form there is very small, gradual decrease in pH for up to 15 minutes; no further change in pH is observed after 15 minutes. The results of water sorption presented in Table 3 show that water sorption of sodium stannosilicate decreases with increasing radius (crystallographic) of the counter ion.

It is quite evident from the IR spectrum plotted in Fig. 2 that the material contains water molecule and metal oxygen bond as is fully discussed below. The structure of sodium stannosilicate is a complicated one like some silicates with other metal ions. An indication of possible structure may be discussed in the light of IR spectrum of the compound. The IR spectrum of the material shows four bands at 3300, 1640, 990, and 700 cm^{-1} regions. In a sample of pure water a strong band is observed at 1630 cm^{-1} and two very strong bands around 3500 cm^{-1}. In the spectrum of the exchanger the band at 3300 cm^{-1} is very strong which can be attributed to O–H stretching frequency. A medium band around 1640 cm^{-1} can be attributed to H–O–H bending band. The O–H stretching bands merge together and is shifted to lower frequency in the spectrum of the exchanger. This is due to possiblity of hydrogen-bonding. In a neat sample of sodium metasilicate there is a very strong and very broad O–H stretching band around 3280 cm^{-1} region and a very strong band around 980 cm^{-1} region due to Si–O stretching frequency. In the spectrum of the exchanger the band around 990 cm^{-1} region can be attributed to Si–O stretching frequency. Since this band is much broader, it can be attributed to Si–O–Si continuous structure. In the spectrum of the exchanger the band around 700 cm^{-1} can be attributed to Sn–O–Sn bridging system.

On the basis of chemical composition and IR analysis the exchanger may be given an apparent formula

$$Na_x(SnO_2)_1(SiO_2)_1 \cdot zH_2O$$

Table 3. Water Sorption on Sodium Stannosilicate in Different Ionic Forms

Serial No.	Counter ion	Ionic radius Å	Water sorbed (g/g)
1	Li^+	0.68	0.4910
2	Na^+	0.98	0.4700
3	K^+	1.33	0.4154
4	Rb^+	1.49	0.3240

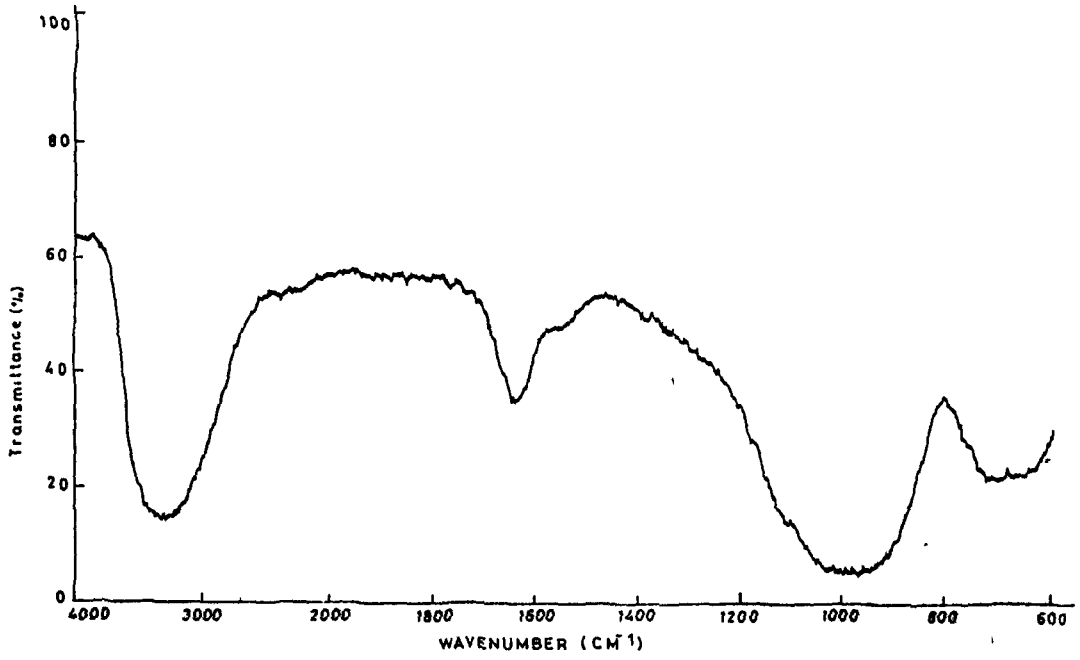

Fig. 2. IR Spectrum of sodium stannosilicate.

Table 4. K_d Values for Some Metal Ions on Sodium Stannosilicate

Serial No.	Metal ion	K_d values / ml g^{-1}	Serial No	Metal ion	K_d values / ml g^{-1}
1	Mg^{2+}	57.14	6	Cu^{2+}	109.09
2	Ni^{2+}	61.54	7	Cd^{2+}	110.00
3	Co^{2+}	75.00	8	Pb^{2+}	133 33
4	Mn^{2+}	83.33	9	Hg^{2+}	400 00
5	Ca^{2+}	90 91	10	Ag^{2+}	3400.00

Table 5. Uptake of Ag^+ by Sodium Stannosilicate from Silver Nitrate Solution of Different Concentrations

Serial No.	Concentration of $AgNO_3$ solution	Volume of solution / ml	mequiv of Ag^+	Uptake of Ag^+ mequiv/0.5 g
1	0.2 M	20	4.0	1.125
2	0.15 M	20	3.0	1.125
3	0.1 M	20	2.0	1.125
4	0.05 M	20	1.0	T.U.[a]
5	0.02 M	20	0.4	T.U.
6	0.01 M	20	0 2	T.U.

a) T.U.; Total uptake of Ag^+.

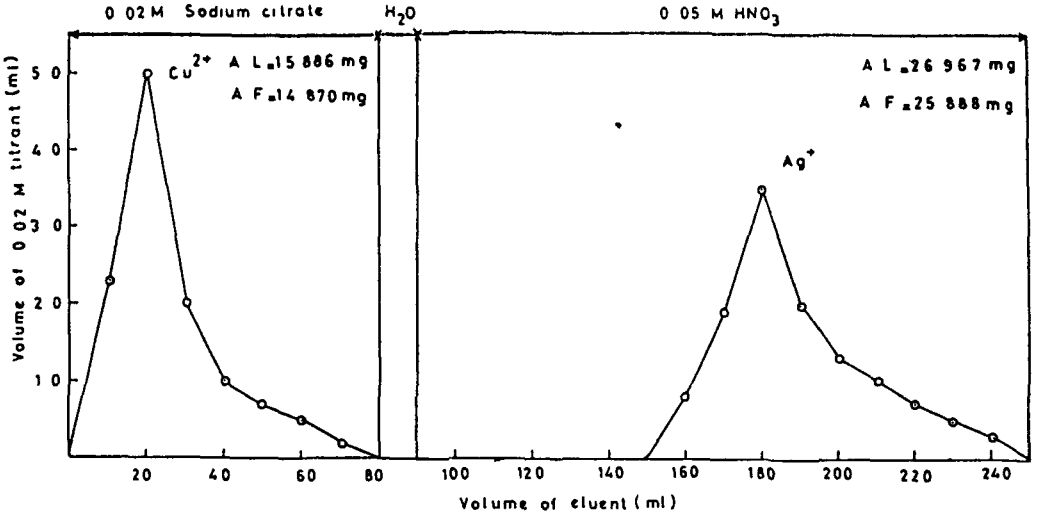

Fig. 3. Separation of Ag^+-Cu^{2+}.
A.L.=Amount loaded, A.F.=amount found.

where z is number of moles of water of hydration.

The distribution coefficient values given in Table 4 suggest the exchanger sodium stannosilicate to be specific for Ag^+. This substance may provide a good method for separation of Ag^+ from other metal ions. Based on K_d values the affinity of different metal ions for the exchanger is

$$Ag^+ > Hg^{2+} > Pb^{2+} > Cd^{2+} > Cu^{2+} > Ca^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+}.$$

Some quantitative separations were achieved on a column of sodium stannosilicate. The order and the eluents are presented in Figs. 3, 4, and 5. These results suggest sodium stannosilicate a useful means of separating Ag^+ from Cu^{2+}, Pb^{2+}, and Hg^{2+} and other fields where the removal of Ag^+ is important.

The results given in Table 5 show that from very dilute solutions, total uptake of Ag^+ is resulted provided that total Ag^+ content of the solution is less than the maximum capacity of sodium stannosilicate. The results of uptake of Ag^+ from solutions containing sodium ion show that the selectivity for Ag^+ is so high that uptake of Ag^+ is not affected by the presence of sodium. This shows the importance of sodium stannosilicate in the recovery of precious metals.

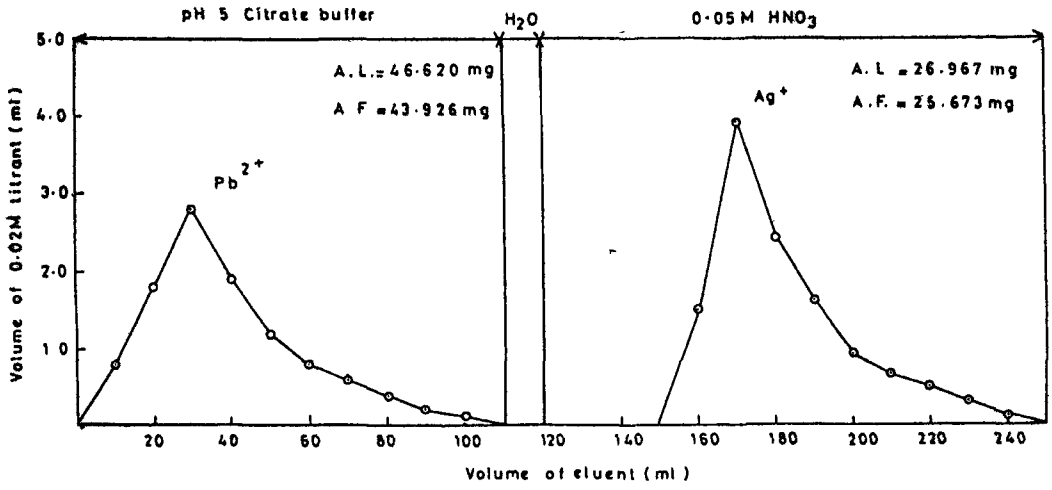

Fig. 4. Separation of Ag^+–Pb^{2+}.
A.L.=Amount loaded, A.F.=amount found.

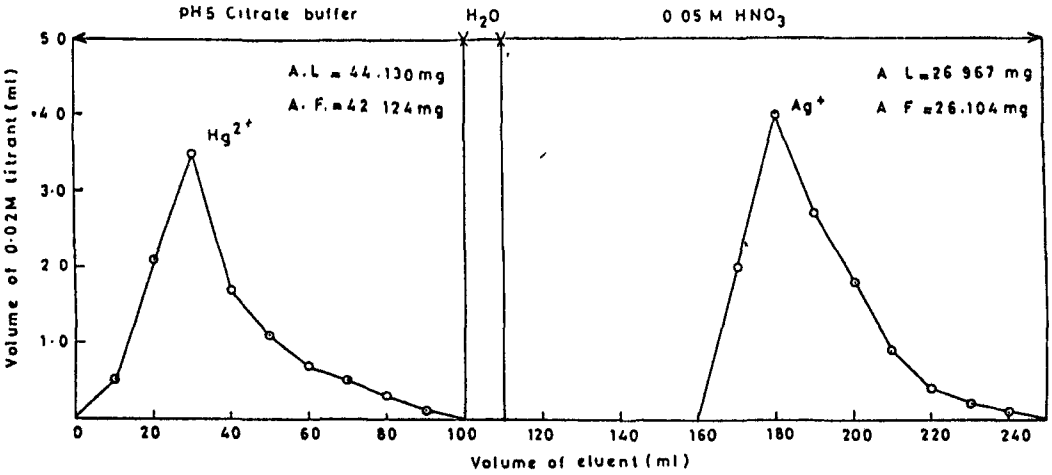

Fig. 5. Separation of Ag^+–Hg^{2+}.
A.L.=Amount loaded, A.F.=amount found.

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